

HYDROGEN SWELLS IN CANNED FRUITS

HIRST

C.F.T.R.I.

CFTRI-MYSORE



3007

Hydrogen swells

ion,

ells,

and packaging

12/28

HYDROGEN SWELLS IN CANNED FRUITS

By F. HIRST and W. B. ADAM

80

Monograph No. 1



March 1937



THE UNIVERSITY OF BRISTOL
RESEARCH STATION · CAMPDEN
GLOUCESTERSHIRE

Printed at The Broadwater Press
Welwyn : Hertfordshire

3007 / G 461

F8,39N:6;Z1

N37

CFTRI-MYSORE



3007

Hydrogen swells

PREFACE

THE six years which have elapsed since the first bulletin on hydrogen swells was published by the Campden Research Station have seen many developments in the scientific and practical study of this subject. In the present monograph special attention has been given to the work carried out in this country, as the problems studied cover a wide field and deal particularly with the fruits grown and canned in England. Direct reference to much of the pioneer work conducted in the United States has thus had to be omitted, though the authors realize fully how much the British canning industry is indebted to the labours of American scientists. Amongst those most responsible for the early theories regarding the corrosion of tin and iron in fruit acids Kohman and Sanborn, Lueck and Blair, and Culpepper and his co-workers are outstanding. The action of sulphur compounds and nitrates was investigated by Clough, Shostrom and Clark, while many valuable practical canning trials were carried out under the direction of G. S. Bohart. References to the original papers will be found in a bibliography given at the end of this publication.

The subject of hydrogen swells is one of pressing importance to the industry, and is a frequent topic for debate at canners' conferences; it is therefore important that a summary of the existing knowledge of the subject, such as is given in the present monograph, should be issued from time to time. The increasing importance of the metallurgical aspects has made it advisable to include a section on fundamental questions relating to corrosion; this section is intended mainly for the chemists and technical experts in the industry, but an attempt has been made to state the scientific facts in such a way that the majority of canners will be able to understand the chief points connected with the subject. The remaining sections have been kept as free as possible from scientific terminology.

The corrosion tests mentioned on pages 48 and 53 were kindly carried out for the authors by Mr. T. N. Morris of

Cambridge, and the copper analyses mentioned on page 47 were supplied by Dr. T. P. Hoar. The authors are also indebted to Mr. Morris and Dr. Hoar for reading the manuscript and offering certain helpful comments. They would also like to refer to the interest taken in this work by Mr. D. J. Macnaughtan, Director of the International Tin Research and Development Council.

CONTENTS

INTRODUCTION	Page 7
INTERACTION BETWEEN CAN AND CONTENTS	8
Staining of the Can; Discoloration of Contents; Cloudiness; Metallic Contamination	
USE OF LACQUERS	14
pH AND ACIDITY	14
PERFORATIONS	17
THEORETICAL ASPECTS OF THE CORROSION PROCESS	19
TINPLATE	20
Composition and Manufacture	
THE CORROSION PROCESS	21
Published Work; Mechanism of Corrosion	
FACTORS INFLUENCING CORROSION	25
Corrosion of Tin; Corrosion of Steel; Corrosion of Tin-Iron Couple; Composition of Steel Baseplate; Porosity of Tin Coating; Effect of Oxygen; Acidity and Addition of Acid; Ac- celerators and Inhibitors.	
PRACTICAL IMPLICATIONS OF LABORATORY STUDIES	34
THE PRACTICAL PROBLEM OF HYDROGEN SWELLS	
SCOPE OF CANNING TRIALS	37
EXPERIMENTAL METHODS	38
EXPRESSION OF RESULTS	40
RELATIONSHIP BETWEEN HYDROGEN SWELLS AND PERFORATIONS	41
Comparisons of Fruits; Sites of Perforations	

TINPLATE	44
Value of Canning Tests; Porosity and Weight of Tin Coatings; Chemical Composition of Baseplate; Strip Plate; Physical Structure; Conclusions	
CANS AND CAN-MAKING	54
Mechanical Aspects of Doming; Damage to Tin Coating; Types of Cans; Lacquers and Lacquering; Protection of Seams	
RAW PRODUCTS	64
Comparison of Fruits; Effect of Ripeness; Holding Fruit before Canning; Strigs in Blackcurrants; Type of Sugar Used; Addition of Acid; Accelerators and Inhibitors	
CANNING PROCESSES	78
Headspace; Exhaust Process; Clinching and Closing Temperature; Cooling	
STORAGE CONDITIONS	81
Temperature; Agitation; Storage in Hot Climates	
CONCLUSIONS & RECOMMENDATIONS	85
GENERAL COMMENTS	85
INDIVIDUAL FRUITS	86
Gooseberries, Strawberries, Raspberries, Loganberries, Blackcurrants, Blackberries, Bilberries, Cherries, Greengages, Golden Plums, Red Plums, Victoria Plums, Damsons, Apples, Prunes, Apricots, Peaches, Pears, Pineapples, Grapefruit, Rhubarb and Tropical Fruits.	
PRECAUTIONS AND REMEDIES	91
Tinplate; Can-Making; Raw Materials; Canning Processes; Transport and Storage	
REFERENCES	93
BIBLIOGRAPHY	95

INTRODUCTION

CANNED foods now hold an important place in the dietary of the urban population of most nations, and have acquired a justifiable reputation for soundness and palatability. It is therefore most desirable that those responsible for the control of public health should have some means of judging from the outward appearance of a can whether its contents are in a fit state for human consumption. No infallible test of this sort exists, but it has long been the custom to view with suspicion any can in which the ends have become convex. Cans in this state are usually referred to as "blown"—the ends having been forced outwards by an internal gaseous pressure—and are regarded alike by canners, retailers and medical officers of health as unmarketable. This pressure is generally assumed to be caused by the production of carbon dioxide gas as a result of fermentation of the contents by yeasts or bacteria, and, though decomposition of this type does not necessarily render the food harmful to health, it is safer to avoid eating any product affected in this way.

Unfortunately for canners, and for all others concerned with the marketing of canned produce, there is another and more dominant cause of doming of the ends of cans. In the case mentioned above the action was biological, the gas formed was carbon dioxide, and the effect on the contents was to make them unfit for consumption ; in the present case the action is chemical, the gas formed is hydrogen, and the effect on the contents is negligible as far as the soundness of the food is concerned. Without a laboratory and the necessary apparatus and experience it is not possible to assign the cause of doming with any high degree of certainty, so domed cans—whether they be due to the processes of fermentation or to the formation of hydrogen by corrosion—must be treated alike and not sold to the consumer. Technical improvements in the sealing of the cans and an increased understanding of the sterilizing process have reduced the losses from "blown"

cans to negligible proportions, but the problem of the hydrogen swell remains.

The object of this monograph is to describe some of the many lines of approach towards an ultimate solution of the difficulties arising from this type of interaction between the container and its contents.

In examining a problem of this nature, two distinct methods may be used, the one based on fundamental and the other on practical considerations. The latter is mainly concerned with providing the best immediate remedy, while the former aims at the ultimate removal of the chief causative factors. Each has its own special scope and limitations, and each has its part to play in the final elimination of this troublesome defect.

INTERACTION BETWEEN CAN AND CONTENTS

It is very rarely that canned products other than fruits form hydrogen swells to such an extent that they involve the canner in heavy financial loss. Hydrogen swells have been recorded in canned vegetables, meats and fish, which have been examined at Campden, but these were all cases of stocks which were several years old, and were not representative of normal packs of these products. In spite of the supreme importance of this problem in connection with canned fruits, it should be regarded as only a part—though a very important part—of the larger problem of the interaction between the container and its contents. Staining of the can and discoloration or metallic contamination of the contents are other aspects which must be considered if the subject is to be viewed as a whole, as it is quite possible to make the situation worse in regard to one defect while improving it as regards another.

STAINING OF THE CAN

The bright appearance of the metal on the inner surface of the can may be tarnished or stained in one of three ways : (a) by excessive corrosion with detinning, (b) by the action of sulphur residues, or (c) by rusting of the metal surface where it comes in contact with the headspace gases.

If a can is not protected by a film of lacquer, the surface of the tinplate may be etched by the fruit acid, and thus lose its uniform bright appearance ; more serious attack may produce severe detinning and the metal may then show dull leaden-coloured patches. Cans in this state present a most unattractive appearance and the contents are generally rather heavily contaminated with tin. The presence of oxygen or oxidizing agents are often responsible for detinning.

Sulphur is frequently used in various forms as sprays or powders in orchards and plantations to safeguard fruit from attack by mildew. When the dusting or spraying is done after the fruits have formed, residues may still adhere at the time of picking, and traces of sulphur may thus gain access to the cans. The reducing action of the corrosion process eventually converts the sulphur compounds to hydrogen sulphide, which stains the cans, imparts a foreign flavour to the contents, and strongly affects hydrogen formation. Amounts as small as two parts of sulphur per million have produced objectionable staining in experiments conducted at Campden. In severe cases the stains produced are brown or black, while the discoloration with non-acid products, such as vegetables, may be in a variety of tints from blue to purple, according to the thickness of the stained layer. Coating the metal with the normal acid-resisting lacquer does not prevent staining by sulphur, and so the only method of avoiding this defect is to exercise special care in selecting and preparing the fruit for canning. -

In the case of non-acid products, such as vegetables, sulphur may occur as a normal constituent of the product itself, and in such cases a special sulphur-resisting lacquer is used. The latter contains a minute quantity of a zinc salt which does not normally diffuse into the contents of the can, but protects the metal surface and forms a colourless compound where the sulphur gases come in contact with it. This lacquer should not be used for acid fruits as the zinc then tends to dissolve out and contaminate the product. The extent of such contamination is extremely small and much below the amount that might be consid-

ered injurious to health, but the food regulations in this country definitely prohibit the presence of zinc in food-stuffs, and for that reason the use of this lacquer for canned fruits should be avoided.

The third type of staining referred to above—namely, internal rusting of the cans—was made the subject of an investigation at Campden a few years ago (12). This discoloration is the result of interaction between the can and the gases of the headspace, and appears to occur in any class of canned foodstuff where the composition of the gases is suitable, irrespective of the acidity of the product. Light or dark brown patches occur where the steel base is exposed, if the ratio of oxygen to carbon dioxide is greater than unity. In most fruits the gases held internally contain a high proportion of carbon dioxide, and the subsequent headspace gases in the canned products have consequently a low oxygen-carbon dioxide ratio and do not stain. Repacked fruits—such as those used for fruit salads—have had most of their carbon dioxide expelled during the first canning process and so tend to bring about staining of the can when they are packed again. A high closing temperature and a small headspace both reduce this staining to a minimum, but where it occurs it may easily be removed by inverting the cans and allowing it to dissolve off. In plain cans the oxygen in the headspace rapidly disappears, and in the course of a few days no further staining can take place. Cans in which staining is liable to occur should be held for at least a week before they are inverted, after which time there is little risk of rust forming on the inner surface of the newly exposed end.

DISCOLORATION OF CONTENTS

Serious discoloration in canned fruits only occurs where there is a soluble natural red or purple colouring matter present. These anthocyanin pigments are found in most of our berries and in many plums; they are very sensitive to the presence of tin and iron, as little as five parts per million of either of these metals producing a notable change in tint. For this reason all our red and purple fruits have to

be packed in lacquered cans. Scratches on the bodies of the cans, or exposed metal on the seams and expansion rings, cause fruits which are in contact to show a blue tint; later and slower action—such as the gradual corrosion which takes place along the seams—does not produce such a strong blue discoloration in newly opened cans. The reason for this appears to be that the staining is more marked when oxygen is present. Subsequent exposure of the canned fruits to the air often increases a state of discoloration which may not have been very noticeable when the can was first opened.

Beetroot is the only vegetable which contains an anthocyanin pigment, and it is necessary to use a well lacquered can for packing this product.

Another type of discoloration in the red and purple fruits is fading or bleaching, which is due to the reducing action of the corrosion process. Raspberries and loganberries fade more easily than other fruits, but the colour is often partially regained when the canned fruit is exposed to the air; the final colour, however, is never as bright as that of the freshly canned product.

Green fruits—such as gooseberries, greengages, and green Pershore plums—tend to turn brown when canned, but in these cases the use of a lacquered can makes this change more noticeable. Gooseberries packed in plain cans have generally a rather better colour than those packed in lacquered cans, and it appears that this is due to the stabilizing action of minute traces of tin which go rapidly into solution during the canning process. Copper and zinc both form bright green compounds with chlorophyll which are stable in acid solution at high temperatures, and experiments have shown that traces of tin in solution can act in a rather similar manner.

General darkening of colour takes place when canned fruits are stored at high temperatures, but this is unconnected with the container in which they are packed. It is purely a matter of temperature, though the action is more pronounced if a trace of oxygen is present.

CLOUDINESS

In some fruits which do not contain a soluble colouring matter, such as gooseberries or golden plums, the syrup after canning may not be quite clear. This is due to the presence of natural colloidal substances such as pectin, and cannot be avoided; but these fruits are often packed in plain cans, and in such cases a slight opalescence is often noticeable. This faint opacity is usually referred to as "cloudiness," and according to Chapman (7) is due to the suspension of tin hydroxide produced by hydrolysis of tin salts of the fruit acids. Opalescence of this nature is not necessarily a sign of excessive metallic contamination, and may occur where the tin content is not more than 50 parts per million. Fruits of all kinds packed in lacquered cans may occasionally show slight cloudiness, but this is seldom present to an extent which makes it readily observable.

METALLIC CONTAMINATION

Tin is not regarded as a poisonous metal, and it is generally considered that very large doses have to be taken to produce serious digestive disturbance. Most of the tin present in canned foods appears to be held in a form in which it is insoluble in the gastric and intestinal juices; consequently it is not absorbed during the process of digestion. Buchanan and Schryver (5) made a careful study of the subject in 1908, and came to the conclusion that quantities of tin in excess of two grains per pound in foodstuffs might render them potentially injurious to health. They put forward a recommendation that this quantity—which is equivalent to 286 parts per million—should be regarded as the upper limit for contamination of foods by tin, and, since the publication of their report, it has been so regarded by the responsible authorities in this country.

The actual quantities of tin normally present in canned fruits and vegetables packed under modern conditions in this country has been the subject of an investigation which has been in progress for nine years at Campden. The amount of tin found in each type of canned fruit and

vegetable and the effect of the method of lacquering and the temperature of storage have been studied, but the full results have not yet been published. Over one thousand analyses have been made during the course of this work, and a few of the more important findings will be mentioned.

The amount of tin removed was found to vary greatly with the type of product packed, some of the vegetables being more heavily contaminated than the most acid fruits. Rhubarb causes rapid detinning of the plate, and must be packed in very well lacquered cans. Lacquering greatly reduces the tin content of all products, most fruits and vegetables showing only ten to thirty parts per million of tin after storage at normal temperatures for twelve to eighteen months. Peas stored in lacquered cans for six years have shown as little as twenty-four parts per million of tin. Gooseberries, greengages and golden plums, if packed in plain cans, may contain about seventy to 120 parts per million of tin, and white cherries about thirty parts per million after a similar period of storage. Most vegetables in plain cans show eighty to 170 parts per million after one to two years' storage, but asparagus may show over twice this amount. Raising the temperature of storage from that of a normal well-ventilated room to 72° F. (constant) increased the average tin content by forty-six per cent in a large range of tests, while raising it to the excessively high temperature of 95° F. (constant) increased the tin content by 170 per cent.

The interesting point about all the tests carried out under normal conditions of canning and storage was that, when lacquered cans were used—and it is the custom to pack most English fruits and vegetables in this class of can—the tin content after a year's storage rarely exceeded thirty parts per million (i.e. about one-tenth of the recognized "limit" for tin in foods) and in some cases was below ten parts per million. If further improvements in lacquering can be introduced so as to ensure complete protection of the entire surface of the cans, it should be possible virtually to eliminate even the minute metallic contamination which exists at present.

USE OF LACQUERS

The effect of various types of corrosion and staining have been discussed at some length as several of the points mentioned have to be taken into consideration when deciding whether or not to use lacquered cans for certain types of fruits. It will be shown later that lacquered cans usually form hydrogen swells much more rapidly than plain cans; they also cost the canner more, and in some cases (e.g. gooseberries) give the fruit a less attractive colour. The question which naturally arises is—What is their advantage?

In the first place, the use of lacquered cans is essential for fruits containing natural soluble red or purple colours; but for the rest, the chief advantages are that the lacquer coating gives the cans an agreeably clean appearance, and that the tin content of the product is kept at a very low figure. When there is any option in the choice of lacquered or plain cans all these factors need to be considered—cost, colour, appearance of can, susceptibility to hydrogen swells, and tin content. The predominance of each factor is not the same for all fruits, so each product packed must be considered as a separate problem.

pH AND ACIDITY

Reference will be made in a later section to the effect of the pH of the contents on the formation of hydrogen swells, and in this connection it might be of interest to give a list of the canned English fruits arranged according to their pH value. Little information has been published regarding the pH and acidity of English fruits, and the following table has been drawn up from analyses conducted at Campden. The figures constitute what is merely a preliminary survey of the subject, and it is hoped shortly to have much fuller data with which to make the comparison between the various fruits. The method of expressing acidity in terms of pH values has been described elsewhere (1).

pH AND TOTAL ACIDITY OF CANNED ENGLISH FRUITS

Fruit	Variety	No. of Samples	pH (Av- erage)	pH Range	Total Acidity
Purple Plums	Purple Persshore	10	2.79	2.69—2.89	per cent. 1.23
Loganberries	—	29	2.92	2.70—3.34	1.29
Golden Plums	Persshore	25	2.93	2.80—3.09	1.01
Victoria Plums	—	17	2.95	2.83—3.07	0.76
Gooseberries	Careless (mainly)	27	2.96	2.72—3.16	1.17
Apples (solid pack)	Various cooking	8	(2.96)	(2.84—3.14)	(0.68)
Damsons	Prune	19	3.01	2.91—3.16	1.38
Blackberries	Cultivated	18	3.03	2.81—3.21	1.04
Raspberries	Lloyd George (mainly)	32	3.04	2.78—3.46	0.83
Blackcurrants	Various	20	3.08	2.82—3.31	1.60
Greengages	—	12	3.14	2.96—3.36	0.78
Cherries(acid)	Morello	2	(3.16)	(3.03—3.23)	(0.83)
Cherries (sub-acid)	Kentish Red, etc.	3	(3.29)	(3.24—3.32)	(0.78)
Strawberries	Various	33	3.42	3.16—3.67	0.50
Cherries (sweet)	White varieties	25	3.86	3.63—4.31	0.25

The pH values in the fourth column were obtained by averaging the results expressed as hydrogen-ion concentrations and reconvertng to pH. The total acidity is expressed as the percentage of citric acid by weight. Where only a few figures were available the results are enclosed in brackets.

Other average pH values recorded in the Campden laboratories are as follows: redcurrants 3.1; bilberries 3.1; rhubarb 3.2; grapefruit 3.35; muscat grapes 3.5; apricots 3.6; peaches 3.7; Cape gooseberries 3.8; mandarin oranges 3.8; prunes (dried prunes blanched and canned) 3.8; pineapples 3.9; pears 4.0; guavas 4.1; mangoes 4.1 (very variable, 3.4 to 4.7 in twenty samples); litchis 4.2; loquats and papaws 5.1. In the case of most of the common fruits mentioned in this list the figures were obtained from ten to twelve samples; in some of the tropical fruits only three or four samples were available for pH determination.

An interesting point arising from the figures in the table is that the ascending order of pH in which they are placed differs considerably from their apparent acidity as judged by most normal palates. If placed in the order of their total acidity (i.e. blackcurrants, damsons, loganberries, Purple Pershore plums, gooseberries, Yellow Pershore plums, . . .) the relative sensations of acidity are more clearly indicated, though they still show anomalies. Varieties of the same class of fruit differ considerably in pH and acidity—examples of this are found in purple plums, with Purple Pershores about pH 2.8, Czars about pH 3.1, and Early Prolifics about pH 3.3; also in cultivated blackberries at pH 3.0, and hedge blackberries at about pH 3.5. Changes in pH on ripening appear to be more noticeable in berries than in plums and may account for the greater range of values recorded in the former class of fruits. Cultivated blackberries, turning from dark red to full black, have been shown to alter in pH from 2.7 to 3.4.

Questions relating to the influence of variety and degree of ripeness on the pH and total acidity of fruits are being studied at Campden at the time of writing.

The pH of vegetables generally ranges from 5.0 to 6.3,

the most acid being some of the stringless beans and the least acid certain types of peas. Tomatoes are usually about pH 4.0 to 4.5.

PERFORATIONS

Dissolution of the steel baseplate always forms part of the corrosion process in canned fruits. This is essentially a localized action and takes place most readily at points where mechanical strains have brought about exposure of steel, notably in the seams and round the expansion rings. The ultimate effect of this attack on the baseplate is to cause perforation of the metal—an action which makes it possible for micro-organisms to enter the can and thus cause spoilage of the contents. In most cases sufficient hydrogen is evolved to bring about doming of the ends before perforation of the metal takes place, and a considerable period usually elapses between the formation of a hydrogen swell and perforation of the can. It occasionally happens that perforation occurs before the ends dome, but this is mainly confined to cases of exceptionally rapid corrosion and to certain types of fruits—notably bilberries.

In the early stages of doming it is usually possible by gentle pressure to cause one end of the can to revert to its concave shape and the other end to dome outwards; in this stage the can is known as a “flipper” or “springer.” Later both ends become convex and the pressure may ultimately be sufficient to make a “hard swell.” Perforation usually takes place about this stage and it is very unusual for a hydrogen swell to burst. Morris (21) has pointed out that this may be due to the fact that hydrogen can pass through tinplate.

The chief sites and frequency of perforations may depend on the structure and composition of the tinplate, on the type of mechanical strains and fractures set up during the fabrication of the cans, and on the nature of the product packed.

In the case of lacquered cans stored under normal conditions in this country, hydrogen swells do not normally appear in appreciable numbers until a year after

packing, and even then they are largely confined to sweet cherries, greengages, blackcurrants and certain varieties of plums. The fact that their first appearance often takes place in the early months of the summer gave rise to a belief—which has not quite died out in some quarters—that the swelling is due to germination of the stones inside the cans. This is not only impossible for the good reason that a biological change of this type cannot take place in the oxygen-free atmosphere inside the can, but can easily be disproved by analysing the gases in the headspace—hydrogen being found in large quantities. The mechanism of the process which causes this gas to form is described in the following section.

THEORETICAL ASPECTS OF THE CORROSION PROCESS

The ultimate aim of all research on the subject of hydrogen swells is to prevent interaction between the metal of the container and the canned material. One method of solving the problem might be to interpose an unbroken film of lacquer between the metal and the foodstuff; this possibility is worth careful study, and will be referred to in a later section of this monograph. All other methods must depend either on modifying the chemical composition or physical structure of the tinplate, or on adding to the canned product some harmless substance which will act as a strong inhibitor of corrosion. The scientific work connected with these last two methods can best be carried out in a metallurgical laboratory, where they can be treated as special problems of metallic corrosion; under these conditions each of the factors influencing corrosion may be studied individually and in the absence of most of the others. Many problems of corrosion have been successfully solved by putting into practice the results of fundamental work of this nature, but it should be emphasized that a considerable time generally elapses before the commercial processes can be perfected. More is required than the mere identification of the chief aggravating factors; their effect must be studied in combination with, as well as in isolation from the rest of the influencing factors; a method of elimination must be found which can be applied in practice without raising the costs of production appreciably; and the results must be sufficiently uniform to justify any serious departure from existing methods of manufacture.

The most satisfactory solution to the hydrogen swell problem seems to be along this line of approach, for it is an attempt to reach the root of the problem. Unfortunately the ideal conditions of the laboratory cannot always be

put into commercial practice on account of increased costs of production, or inability to overcome technical difficulties connected with commercial processes. It may be, therefore, that other methods will have to be adopted to solve the immediate problem of the hydrogen swell ; meanwhile we can only hope that the fundamental researches at present in hand will meet with ultimate success.

TINPLATE

COMPOSITION AND MANUFACTURE

Tinplates are sheets of mild steel about 0.012 inch in thickness, coated with a thin layer of almost pure tin. The two standard weights of tin coating in general use are known as "coke" and "charcoal" plate respectively ; the former contains about 28-ozs. and the latter an additional 8-ozs. or more of tin per base box of plates. Cans are made almost entirely from coke plates, and in these the thickness of the tin coating is roughly 0.0001 inch.

The chemical and physical properties of the steel base-plate are greatly influenced by the total percentage and method of distribution of the substances other than iron which are present. The percentages of these "impurities" in the iron vary considerably in different lots of steel, but are roughly as follows : Carbon 0.05-0.14 ; manganese 0.34-0.42 ; phosphorous 0.04-0.07 ; sulphur 0.03-0.08 ; copper 0.005-0.18 ; silicon 0.006-0.02 ; nickel, trace to 0.05 ; chromium, trace to 0.05.

The steel bars from which the plates are made are first subjected to a process of "hot rolling," each length being folded over on itself until it is generally eight sheets thick when cut. The sheets are separated and the surface freed from oxide by "pickling" in dilute acid ; they are then "black annealed," when the final crystal structure of the iron and the distribution of the other substances are largely determined. The next process is known as "cold rolling" and is followed by a second annealing at a lower temperature than the first in order to remove the strains set up in the metal. A second pickling in dilute acid is given and the plates are held in water very slightly acidified with sulphuric acid till they are required for tinning,

when they pass first through flux and then through the tinpot and grease-pot. On emerging they are cleaned—generally by means of bran, but sometimes by treatment in a soda-bath—and finally “assorted” during which operation plates containing visible imperfections are removed.

The tinplate as finally produced does not consist of a central layer of steel covered by a sharply defined coating of tin on either side. In between the two metals there exists an intermediate layer of a tin-iron compound containing about one-eighth of total tin in the tinplate ; this layer will be referred to again later.

THE CORROSION PROCESS

PUBLISHED WORK

Most of the earlier work on the causes of hydrogen swells was carried out in the United States, and consisted of practical experiments designed to indicate the factors chiefly responsible, and to demonstrate how losses might best be reduced to a minimum. A careful study of the effect of various impurities in the steel baseplate was made along these lines in 1917 and 1919, but the results—which were published in a bulletin issued by the National Cannery Association (29)—were rather inconclusive, though they did appear to indicate that copper up to 0.3 per cent exercised an inhibiting action on steel corrosion. It is only within the last eight or ten years that the fundamental basis of the problem has been investigated, and in this connection the work of Kohman and Sanborn, Lueck and Blair, Culpepper and Moon, and Mrak and Richert in America is outstanding.

Work on the fundamental problem of corrosion of tinplate in fruit acids was begun at the Low Temperature Research Station at Cambridge in 1927, and special reports on the subject, written by Morris and Bryan (19, 20) were issued in 1931 and 1936. Further investigations have recently been conducted in England, largely as part of a programme of work undertaken by the International Tin Research and Development Council. In writing this brief account of the theoretical basis of tinplate corrosion

the present authors have made full use of the published accounts of the work referred to above.

MECHANISM OF CORROSION

For a clear understanding of the corrosion process the reader should study one of the several excellent textbooks published on this subject. The short description given below cannot be other than inadequate, but some knowledge of the mechanism of corrosion is necessary if the fundamental aspects of the hydrogen swell problem are to be appreciated. It is impossible to offer any such explanation without making use of the terminology associated with the subject, and in the following paragraphs it has been assumed that the reader has some knowledge of general scientific terms.

Corrosion is an electrochemical process, and involves the passage of metals to and from the uncombined metallic state and the dissolved or *ionic* state. When a metal is immersed in a solution containing its own ions, there will be only one potential at which equilibrium can exist between the metal and its ions in the solution; this value, expressed in volts, is called the *equilibrium potential* for the particular metal under the conditions ruling. This potential cannot be measured directly, as a metal immersed in a solution of one of its salts only forms what is known as a "half-cell." The measurement is actually made by first connecting this half-cell to another of which the potential is already known, and then finding the E.M.F. of the complete cell by means of a potentiometer. All such comparisons are referred to a standard known as the *normal hydrogen electrode*, which consists of a strip of platinum coated with platinum-black saturated with hydrogen at one atmosphere pressure and immersed in a solution which is "normal" in regard to hydrogen ions. The arrangement of a cell of this type can be indicated in the manner shown below, the two solutions generally being joined by some suitable connecting liquid.

Metal		Metallic ions in solution		Hydrogen ions in solution		Platinum saturated with Hydrogen
-------	--	---------------------------------	--	---------------------------------	--	--

If the two electrodes are brought into contact a current will tend to flow in one direction or the other. The E.M.F. of this current can be measured by balancing it exactly against a known E.M.F. produced by a standard battery, and adjusted by means of a potentiometer. As all equilibrium potentials are referred to that of the normal hydrogen electrode it is convenient to take the latter as zero in this scale of measurement. If the various metals are now arranged in the order of their normal electrode potentials, as expressed on the hydrogen scale, they form what is known as the *Electrochemical Series*. The order is found to be as follows :

Gold, platinum, silver, copper, (hydrogen), lead, tin, nickel, cobalt, iron, zinc, aluminium, sodium, potassium.

It will be seen that hydrogen occupies a position towards the middle of the series ; the significance of this fact may be shown by comparing the behaviour of one metal above it in the series with one below—silver and tin can be taken as examples. When the normal electrodes of silver and hydrogen are connected in the form of the cell shown above, a current tends to pass in one direction ; in this case (as with all metals above hydrogen in the list) the passage of the current is accompanied by a transference of hydrogen from the gaseous to the ionic state at the hydrogen electrode, and of silver from the ionic to the metallic state at the silver electrode. If an external E.M.F. is applied so as exactly to balance that of the cell, its value (in this case about 0.80 volts when no current passes either way) will represent the electrode potential of silver. Any further increase in the applied E.M.F. will bring about a reversal in the direction of the current, with the result that silver dissolves from its own electrode and hydrogen is released at the hydrogen electrode. The electrode at which dissolution (i.e. passage *to* the ionic state) takes place is termed the *anode*, and that at which deposition of the metal or evolution of hydrogen (i.e. passage *from* the ionic state) occurs is called the *cathode*. In the case of silver it will be observed that the metal is cathodic to the hydrogen electrode. Turning to the case

of tin (or any metal below hydrogen in the series) it will be found that an opposite state of affairs exists, the metal being anodic to hydrogen and therefore suffering dissolution.

It is customary to give positive values to the electrode potentials of those metals above hydrogen in the series (hydrogen being zero) and negative values to those below. When any two metals are connected in the manner described the higher member forms the cathode and the lower the anode; deposition takes place on the former and dissolution on the latter. The highest members of the series are thus not easily corroded and tend to favour the metallic state; these are known as the *Noble Metals*. The lower members, on the other hand, are characterized by their highly reactive properties, and the relative ease with which they are corroded. Tin and iron are the two metals with which we are concerned in the problem of hydrogen swells, and it might be expected, from the considerations mentioned above, that the tin would act as cathode and the iron as anode, the latter metal being the one which underwent dissolution. This question—the corrosion of the tin-iron couple—will be dealt with more fully in a later section.

If we now turn to the question of two metals immersed in dilute acid and brought into contact, we find that dissolution takes place on the less noble of the two (the anode), while hydrogen ions are forced towards the more noble where they pass into the gaseous state and are released as hydrogen gas. Some metals when acting as cathodes offer conditions which are unfavourable to the change of hydrogen from the ionic to the gaseous state; in such cases the potential difference between the electrodes may have to be raised considerably before evolution of hydrogen takes place. This margin between the equilibrium potential and that at which bubbles of hydrogen are first released is often called the *overvoltage* or *overpotential* of the metal. In modern practice overvoltages are generally expressed in relation to particular rates of hydrogen discharge.

In the case of the two metals in dilute acid referred to

above, we can now consider what happens when the electrochemical action is set up between the two metals and a current starts to flow in one direction. This would continue steadily and cause severe corrosion to take place at the anode ~~it~~ ^{if} were not for one counteracting factor, namely that the hydrogen which is evolved at the cathode tends to remain in contact with the metal, thereby reducing the active area of this metal. The current is thus checked or stopped. This action, which is of great importance in problems connected with corrosion, is known as polarization. The extent of the reduction of the current is influenced by several factors of which the difference in electrode potentials of the two metals and the cathodic overvoltage are the most important. The layer of hydrogen which protects the cathode can be gradually removed by traces of oxygen or oxidizing agents present in the solution ; depolarizing agents such as these thus hasten the process of corrosion.

Single metals such as steel can undergo rapid corrosion when immersed in dilute acid. This is due to the fact that a large number of points on the surface can act as cathodes while others can form anodes. The structure of the metal, the roughness of the surface, and the presence of crystals of certain metallic impurities are all factors which influence the release of hydrogen, and thus affect the efficiency of the cathodic process.

FACTORS INFLUENCING CORROSION

CORROSION OF TIN

If the inner surface of cans consisted of an unbroken coating of tin then the facts relating to the corrosion of this metal would be of great importance in connection with the problem of hydrogen swells. As it is, discontinuities always exist in the tin coating, and the situation is altered by the presence of iron. Tin itself is not readily attacked in the absence of air, but when oxygen is present dissolution can be rapid. Tin is easily polarized, and the action of oxygen or oxidizing agents is to bring about depolarization, and thus accelerate the corrosion process. The corrosion of tin tends to decrease as the acidity rises.

Contact with iron increases the rate of corrosion of tin in dilute acid. The effect of minute impurities in the metal is not yet fully understood, but it seems probable that traces of antimony and bismuth tend to slow down the process of corrosion.

The action of various metals in solution on the corrosion of tin has been studied by Bryan (3) who has shown that the ferrous ion can act as a carrier of oxygen and bring about increased corrosion of tin. This means that one of the products of corrosion of the tin-iron couple increases the rate of corrosion of the tin coating by the oxygen present, thus tending to lay bare more of the steel base. The greatest effect is at pH 3. Using a constant pH of 2.4, Bryan found that the rate of corrosion of tin in a limited supply of oxygen was not greatly affected at first by concentrations of ferrous ions as low as two parts per million; the effect rapidly became more pronounced as the concentration was raised to twenty parts per million, but the extent of the final corrosion in all cases was the same. Absorption of oxygen after the corrosion was complete took the form of converting stannous to stannic ions.

CORROSION OF STEEL

The mild steel used for making tinplates corrodes rapidly in dilute acid, both in the presence and absence of oxygen. The effect of oxygen is more noticeable at low acidities. In slow-corroding steels fully exposed areas of the metal tend to be attacked when the acidity is relatively high, and less exposed areas (such as might be found in the seams of cans) suffer corrosion when the acidity is low. Contact with tin very considerably decreases the corrosion of steel, the rate of dissolution of iron decreasing as the area of tin is increased.

The presence of tin ions in the corroding medium inhibits the corrosion of iron, while sulphur compounds act in the opposite manner as accelerators. The action of tin ions is most noticeable when corrosion is rapid, and sulphur compounds have their maximum effect when the normal corrosion is slow. Hoar and Havenhand (10) have shown that sulphur compounds react at the anode to form

hydrogen sulphide, which reduces anodic polarization and thus stimulates corrosion. They consider that the beneficial action of tin ions in the solution is due to the fact that they remove traces of hydrogen sulphide (caused by sulphur present in the steel) in the form of insoluble stannous sulphide and so tend to increase anodic polarization.

The composition of the steel baseplate is almost certainly the most important single factor in connection with the hydrogen swell problem, and will be referred to more fully in a later section.

CORROSION OF TIN-IRON COUPLE

In plain cans the metallic surface exposed consists of a large area of tin and a very small total area of steel, the latter being mainly found in the seams and round the expansion rings. If we refer back to the list of metals known as the Electrochemical Series (page 23) we find that tin is more noble than iron, and consequently we may expect iron to dissolve when the two metals are coupled together in a dilute acid medium. If these conditions were to hold true in the case of canned fruits, then the full effect of the corrosive action would be concentrated on a very small area of exposed iron, with the result that rapid perforation of the metal might be expected. In practice, it is found that tin rapidly becomes anodic to iron under the conditions existing in canned fruits, and so prevents excessive corrosion of the exposed steel. This reversal of potential has been accounted for in a variety of ways, and has been attributed by Lueck and Blair (17) to the high overpotential of tin (page 24), which, by its reluctance to release hydrogen as gas, leaves the iron as the only avenue of escape. Another explanation has been put forward recently by Hoar (9) who considers that two stages occur in the electrochemical relationships between tin and iron immersed in fruit acids: (1) the two metals initially exhibit an enhanced nobility due to the presence of oxide films on the surface, but these films rapidly break down, leaving the bare metals exposed; and (2) the normal relationship existing between tin and its ions in the immedi-

ate vicinity of the tin electrode is upset by the removal of the ions as complexes formed with the fruit acids. This latter action reduces the potential of the tin electrode to a point below that of the iron, and hence reverses the direction of the current.

No matter what explanation is finally accepted the important fact remains that this reversal of potential does take place in canned fruits ; the tin being anodic tends to go into solution, while the areas of exposed iron being cathodic form the points from which hydrogen is evolved.

It has been mentioned previously that the steel base itself can suffer corrosion in dilute acid, certain points acting as cathodes and others as anodes. This process continues even when the steel is in contact with tin, but the condition in plain cans is such that the proportion of tin to steel is very great. If we imagine the small areas of exposed steel first uncoupled and then coupled to the surrounding tin we find that the effect of coupling to the tin is to reduce very greatly the anodic dissolution of iron which was taking place previously. The cathodic points on the steel remain the same as before, but the anode now consists of a large area of tin in addition to the minute area of anodic iron previously exposed. The anodic dissolution is therefore no longer concentrated on the iron, and the tin thus affords cathodic protection to the exposed steel.

In lacquered cans almost the whole of the tin surface is protected by the lacquer, and the areas where the tinplate is not completely covered are those where mechanical strains have caused exposure of the steel. The type of corrosion occurring in lacquered cans tends therefore to approximate to that of the steel base rather than to that of the tin-iron couple, as exemplified in plain cans ; there is relatively little anodic protection by tin, and the inhibiting effect of tin ions in the corroding solution is less pronounced owing to the fact that their concentration is less in the lacquered can. Both these effects help to account for the more rapid formation of hydrogen in lacquered than in plain cans, and show the importance of using a satisfactory type of steel for the baseplate.

COMPOSITION OF STEEL BASEPLATE

Mention has already been made (page 20) of the common impurities found in the mild steel used for making tinplates. Of these, carbon, silicon, manganese, chromium, nickel, and arsenic seem to have little effect in accelerating or inhibiting the corrosion of the iron.

Morris (28) has pointed out that the rate of corrosion of different steels in dilute acid under similar conditions varies very greatly, and offers a suggestion—based on the results he obtained—that the sulphur content of the steel might be partly responsible for the effects observed. A study of the action of sulphur was later undertaken by Hoar and Havenhand (10) who showed that sulphides contained in the steel are reduced to hydrogen sulphide at the corroding surface; this diminishes anodic polarization, and thus stimulates corrosion. These workers emphasize the importance of this impurity in the steel, and attribute the beneficial effects of tin ions and copper to their powers of removing sulphur from its sphere of action in the form of acid-insoluble sulphides. They regard copper as a very useful “antidote” to sulphur, and recommend that the copper content of steels used for tinplate should not be less than twice that of the sulphur. It is worth noting in this respect that McConkie (18) has shown, by means of practical canning tests, that amounts of copper exceeding 0.5 per cent appear to increase the rate of corrosion of cans; steels of low copper content, however, were not tested.

Phosphorus has long been suspect as an agent which accelerates corrosion, but very little satisfactory evidence has been brought forward to indicate definitely that this substance produces harmful results. Hoar and Havenhand admit that crystals of iron phosphide might possibly act as efficient cathodic points and thus hasten corrosion, but this fact has not yet been proved. Inclusions of massive cementite (a compound of iron and carbon) appear to form the points from which hydrogen is most readily released, and probably constitute some of the main cathodic areas in the corrosion of the tin iron couple.

The question of distribution as well as the total percen-

tage of impurities is obviously of considerable importance as the earlier stages of corrosion are confined very largely to the surface layers of the steel base. For this reason Hoar and Havenhand recommend the use of "rimming steels" (i.e. steels in which the outer portions are relatively free from impurities) for tinplate; other recommendations are a low sulphur content, a copper-sulphur ratio greater than two, and freedom from massive cementite.

POROSITY OF TIN COATING

Considering the extraordinary thinness of the tin coating on the surface of the steel base, it is not surprising to find that it often lacks continuity. In a paper recently published, Hothersall and Prytherch (15) have shown that the imperfections are mainly of three types—"grease marks," "scruff bands," and "transverse ripples." The first of these consist of depressions in the tin coating connected by narrow channels in the direction of tinning; they are surface tension phenomena, and are produced when the plate leaves the grease-pot. The second are narrow bands containing small crystals of the tin-iron compound FeSn_2 , and are caused by uneven movement of the plate through the tinpot. The last are narrow channels in the tin coating running roughly at right angles to the direction of tinning. These are all lines of weakness in the tin coating, and form the sites of actual or potential pores. Porosity is reduced if a thicker layer of tin is used, provided other factors remain the same, and so charcoal plate tends to show fewer areas of exposed steel than coke plate. Scratching of the plate during cleaning or subsequently is responsible for a large proportion of the pores normally found.

The material immediately below the tin coating consists of a tin-iron compound FeSn_2 , and consequently the properties of this intermediate layer are of some importance in connection with the question of porosity. Hoare (11) has shown that the layer is brittle and easily fractured when the tinplate is bent, while Hothersall and Bradshaw (14) have pointed out that it is very porous; it gives, therefore, very little protection to the steel base under the

conditions which most readily cause the latter to be exposed. Relatively large crystallites of the same tin-iron compound are sometimes found imbedded in the tin coating; these have not been formed *in situ*, but have been picked up in the tinput during tinning.

Tinplates which show a high porosity tend to produce hydrogen swells more readily than those which are coated with a more uniform layer of tin; but it will easily be realized that the question of porosity is less vital in lacquered than in plain cans. In the former type the surface of the plate is almost completely covered by a layer of lacquer, leaving only the damaged areas round the seams and expansion rings exposed to the action of the fruit acids. In the latter type scratches and pores in the tin surface form additional sites for corrosion, and the fewer there are the greater will be the service-life of the cans.

EFFECT OF OXYGEN

It has been mentioned previously that oxygen greatly accelerates the corrosion of tin, but does not produce such marked effect on iron. In the tin-iron couple its accelerating effect is more noticeable at pH 4 than at pH 3, and it mainly hastens the removal of tin.

Horner (13) has shown that the gases held in the tissues of fruits are practically free from oxygen, consequently the oxygen found in the headspace gases is derived from air held mechanically at the surface of the fruits or entrapped above the surface of the contents when the lid of the can is spun on. These facts indicate the importance of an efficient exhaust process.

The oxygen present in the cans when closed rapidly disappears on storage; it is generally no longer detectable after about a week in the case of plain cans, and four to six weeks in the case of lacquered cans. Its chief action is to bring about depolarization.

ACIDITY AND ADDITION OF ACID

The effect of acidity on the incidence of hydrogen swells constitutes a problem which is imperfectly understood as far as its theoretical aspects are concerned. Cherries, at

pH 3.7 to 4.3, form hydrogen swells rapidly, and certain of the more acid fruits, such as gooseberries at pH 3.1, give little trouble in this respect. That the effect is not entirely associated with the pH will be shown in a later section dealing with the practical canning trials carried out at Campden, and it can only be said at the moment that certain fruits of low acidity, such as cherries, benefit by the addition of a small quantity of a fruit acid to the syrup used in canning. Parallel tests with other fruits of similar pH show that the beneficial effect appears to be specific to the fruit rather than general to all fruits of the same acidity.

Hoar (9) has demonstrated by means of laboratory tests on strips of tinplate in corroding media that there is very little systematic difference in the rate of corrosion at pH 2 and pH 5 when air is present. In the absence of air, however, tin and iron both corrode more rapidly at the *higher* acidity. Hoar and Havenhand (10) have also pointed out that the steel baseplate corrodes much more rapidly at pH 2.0 than at pH 4.9. Morris and Bryan (19) found that, in the absence of air, the total corrosion of strips of tinplate in buffered citrate solutions decreased as the acidity fell from pH 3 to pH 5.5, but that the corrosion of tin rose to a maximum, and that of iron to a minimum at about pH 4. When using fruit juices as the corroding media Morris (22) reported that cherries at pH 4.0 to 4.2 actually removed more iron and less tin than any of the other fruits of higher acidity. These apparently contradictory results would appear to confirm the suggestion that some other factor is coupled to that of low acidity in producing the effects recorded in practical canning tests. The disagreement between the results obtained in laboratory tests on buffered solutions and those obtained with the fruit juices themselves also serve to emphasize the need of conducting tests with "all factors present" as well as those designed to indicate the effect of isolated factors.

The fact has already been mentioned that beneficial results are obtained by adding a small quantity of a fruit acid to the syrup used in canning sweet cherries. Morris and Bryan (20) have recently studied the effects produced

by a number of different acids and their conclusions can be stated briefly as follows :

(1) The hydroxy-acids—lactic, tartaric and malic—of the same normality have about the same corrosive powers as citric acid on the metal tin ; tin is not attacked by the non-hydroxy acids, acetic and succinic. The action of citric acid on mild steel is rather less than that of tartaric, and rather more than that of acetic ; malic and citric acids give very similar results. Tartaric acid attacks the steel in tinplate rather more rapidly than citric. Acetic acid attacks the steel member rather severely, but has little effect on the tin.

(2) Oxalic acid has a very strong action on tin, coating the latter eventually with a layer of tin oxalate ; the effect on mild steel is to produce a deposit at pH 3 which checks corrosion, but at pH 4 the deposit ceases to be protective. These results are important in connection with the type of corrosion occurring in canned rhubarb. At pH 2.4 and 3.1 the steel member in tinplate was found to be protected, but at pH 4 corrosion took place.

(3) Experiments with hydrochloric acid show that the chlorine ion has no specific effect on the corrosion of mild steel.

ACCELERATORS AND INHIBITORS

Of the various accelerators of corrosion sulphur compounds at high acidities are the best known ; the effect of these substances on the electrochemical process has been mentioned in a previous section (page 26). Oxidizing agents also tend to hasten corrosion by their depolarizing action, and other substances which can act as hydrogen acceptors produce similar effects—the natural colouring matters of fruits, known as anthocyanins, are substances of this type. Cane sugar, in certain cases, seems to act as an accelerator of corrosion, and in general it is recognized that fruits packed in a sugar syrup give heavier losses from hydrogen swells than those packed in water. Morris (23) has studied this point in some detail, and has found that sucrose acts as a weak inhibitor of the acid corrosion of mild steel, while Bryan (4) has pointed out that it acts as a

fairly strong inhibitor of the corrosion of tin in the presence of air. It does, however, reduce the inhibiting power of tin salts on the corrosion of iron, and this—taken into consideration with the reduced corrosion of tin which it brings about—may account for the increased hydrogen formation in cases where the proportion of exposed iron to exposed tin is high (e.g. in lacquered cans).

Beet sugar has been shown by Morris and Bryan (19) to contain substances which greatly reduce the action of citric acid on mild steel, and the same workers claim that invert sugar can also act as an inhibitor.

Sulphur compounds are known to act as inhibitors where the acidity is low, but here again the controlling factor is not merely the pH of the medium. An explanation of these facts is made more difficult owing to the present disagreement between the results of laboratory tests and those of practical canning trials. Morris (24) has demonstrated that the accelerating effect of sulphur on mild steel diminishes as the acidity of the corroding medium falls, but has not found any inhibition within the pH range 2.4 to 4.5 in laboratory corrosion tests. He suggested that the definite inhibiting action noticed at still lower acidities was due to the formation of a film of iron sulphide on the surface of the steel.

Tin ions are known to be strong inhibitors of the corrosion of the steel baseplate, and their probable action has been described on page 26.

Other possible inhibitors of corrosion are to be found in certain substances—such as gelatine, agar-agar and pectin—which form colloidal solutions. These substances are carried over to the cathode and adsorbed on the surface, thus reducing its efficiency and retarding corrosion; they can also be adsorbed on anodic areas. Morris (25) has shown that the adsorption of gelatine was greater at the higher acidities and that this substance exhibited its maximum inhibiting effect at pH 3.0.

PRACTICAL IMPLICATIONS OF LABORATORY STUDIES

The recent investigations on the mechanism of tin-

iron corrosion have made it possible to account for a number of known facts concerning the formation of hydrogen swells and, in some cases, have shown the way in which improvements can be made. Some of the more important points dealt with are summarized below.

(1) The causes of porosity in the tin coating have been studied and it should be possible eventually to modify certain of the existing processes so as to effect considerable improvements. Further knowledge of the structure and reactions of the tin-iron layer should help to give a clearer picture of the corrosion process.

(2) The importance of the composition of the steel baseplate has been clearly shown. Rimming steels have been recommended for tinsplates together with a low sulphur content, a copper-sulphur ratio greater than two, and freedom from inclusions of massive cementite.

(3) The advantages of plain over lacquered cans have been shown to be mainly due to the protection afforded to the anodic portions of the iron by the large area of anodic tin, together with the inhibiting action of tin ions. This form of protection is more readily effected in plain cans.

(4) The effect of oxygen and oxidizing agents is to increase the attack on the tin surface and to hasten corrosion by causing depolarization.

(5) The accelerating effect of sulphur compounds is explained by their action of diminishing anodic polarization.

Although these scientific studies have only been in progress for a relatively short period, considerable knowledge of the fundamental aspects of tin-iron corrosion has been obtained. The investigations connected with the composition of the steel used for making tinsplates are still incomplete, and it remains to be seen how far it is possible to put the recommendations effectively into practice. Such problems as the effect of acidity on hydrogen formation and the effect of sulphur compounds at low acidity are still incompletely understood, the laboratory tests giving results which are notably different from those obtained in practical canning tests.

An attempt has been made to show the present position in regard to the main process of tin-iron corrosion as viewed from its scientific standpoint. In the succeeding sections of the monograph the problem will be looked at from its practical aspect, and an effort will be made to show to what extent losses from hydrogen swells can be controlled by proper adjustment of existing processes or by modifications which can be introduced as practical measures with the least delay.

THE PRACTICAL PROBLEM OF HYDROGEN SWELLS

SCOPE OF CANNING TRIALS

The hydrogen swell problem is essentially a practical one, and all improvements—whether they be the result of experiments in metallurgical laboratories or elsewhere—must finally be expressed in terms of increased marketable life of the cans. This can only be done by actual canning trials—that is to say, the tests must be conducted with “all factors in.” Such canning tests should not be delayed until the scientific work has been completed and the practical difficulties of improving the resistance of tinplate to corrosion overcome, for in the meantime losses from hydrogen swells will continue to occur and the reputation of the industry as a whole suffer through this serious form of deterioration of its products.

It has been mentioned earlier that the study of the fundamental scientific problem of the corrosion of cans in fruit acid media was begun in this country in 1927, when Morris and Bryan started their work at the Low Temperature Research Station at Cambridge. It was realized, however, that there was a more immediate problem needing investigation as well, and trials were commenced in the same year at Campden to determine how serious the problem was likely to be in connection with our own type of fruits and to what extent the various processes could be modified so as to reduce losses to a minimum. The imperfections of the tinplate in general use at the time had to be accepted, and other means of effecting improvements studied. In this connection over 500 controlled canning tests were carried out at Campden during the years 1927 to 1935, and the summarized results, expressed in the paragraphs below, show the way in which can-makers, canners and those connected with the selling of the goods, can help to reduce the present scale of losses. Recent tests have

given distinctly hopeful results, and the improvements thus imparted to the storage properties of canned fruits should yield great benefits to the industry if they can be effectively put into practice within the next year or two.

EXPERIMENTAL METHODS

The average rate at which hydrogen swells form in cans stored under normal conditions in this country is slow, and tests carried out at these storage temperatures sometimes take four years or more to complete. When cans are exported to countries where the stores are much warmer, the problem becomes a more serious one, and it is sometimes the case that the cans form hydrogen swells very shortly after they reach tropical countries, or even while they are still on board ship on the way out. It was chiefly in order to study the rate of formation of hydrogen swells under conditions of warm to hot storage that the cans packed for the trials at Campden were stored in constant temperature rooms at 72°F. and 95°F. Storage at the lower of these temperatures was abandoned after two years on account of the long time (sometimes over three years) before results could be obtained. The urgency of the problem also made the use of the higher temperature desirable, as it enabled tests to be carried out on improved methods each season. The decision to use 95°F. as a standard temperature for the tests was not taken without realizing that the results obtained under these conditions might be misleading when applied to normal temperatures, as relations which exist between test cans and their "controls" at the severe tropical heat of 95°F. may be very different from those which exist under temperate conditions of storage.

This latter point was to some extent cleared up in the tests carried out during the first two years, when batches of cans of each class of fruit were divided into two lots, one being stored at 72°F. and the other at 95°F. The fruits in each lot fell into virtually the same order when compared later for the relative rates with which they promoted the formation of hydrogen swells, the lot stored at 72°F. showing a marketable life about three times that of the lot held at 95°F. It was noticed that this factor was slightly

lower where rapid hydrogen formation occurred, and slightly higher where corrosion was slow. It is improbable that the use of tropical rather than temperate storage conditions introduces errors which cause a wrong picture to be obtained of the relationships existing at the lower temperatures, but the only way of proving this would have been to repeat all tests at the two temperatures—a proposition which was considered quite impracticable at the time.

In all the trials carried out the main object was to keep constant every factor except the one to be studied. The normal variability of the raw materials used is great enough to produce serious discrepancies in the results unless suitable precautions are taken, and for that reason the following method of procedure was adopted.

In all tests “controls” were packed at the same time and from the same batch of fruit as that used for the test cans. The cans were arranged at random in blocks of forty to fifty for each test—any showing visible defects not being included. It was noted that the condition of the fruit in a consignment often varied considerably, even though obtained at one picking from only one orchard or plantation; a variation was often noted between one chip basketful and another, and to prevent such differences affecting the results, the contents of each basket were distributed so that the fruit was spread equally over each block of test cans. Random distribution was considered unsatisfactory under the conditions ruling. The cans were filled with syrup at 170° F. on a sloping board, which gave them approximately equal headspaces, and were subjected to standard conditions of exhausting, closing, cooking, and cooling. Before passing under the seaming-head of the closing machine the headspace was finally standardized by the action of suitably adjusted displacement toppers. At least three fruits were used where possible for each test, and the close agreement in the results in all except a very small proportion of the trials tended to indicate that interfering factors were not prominent.

The cans were placed in the constant temperature store during the first week in September each season, and were

examined individually each week for development of hydrogen swells or perforations.

Except in a very few cases the size of can used in these tests was the A2.

EXPRESSION OF RESULTS

The simplest method of comparing the results of tests such as these is to plot curves showing the "percentage loss" against "time of storage." This method is the best one to adopt where the number of curves is small, but is not suitable where a large number of tests have to be compared. In the present case it is more convenient merely to indicate in figures by means of tables certain points on the curves. It is rather more usual to take several storage times and compare the percentage of hydrogen swells after these periods, but an alternative method is to take several fixed stages in the development of the hydrogen swells (such as 15, 25, and 50 per cent losses), and compare the times taken to reach these stages. The latter method is the more accurate where the rate of loss is high, as it is in the present case, and so has been used in expressing most of the results in this section of the work.

In any large batch of cans there are generally a few less satisfactory than the main bulk, and also a few which are distinctly better than the average. The rate of loss from hydrogen swells tends therefore to be slow at first, to increase rather rapidly, and then to die off when only a few per cent remain undomed. The most important part of the curve as far as the canner is concerned, is its early stage when the first warning of trouble appears. After 10 to 15 per cent of losses have occurred the rate generally rises rapidly, and so the fixed stages in "storage life" chosen for the tables below were at 15, 25 or 50 per cent loss. It was found that the "25 per cent loss" period served for the purposes of comparison in most cases, and consequently this stage has been used freely to express the results in this section. The percentage losses in all cases include perforations which took place before doming as well as hydrogen swells.

The results of the canning trials shown below have been

grouped into six sections—the first dealing with the relationships between hydrogen swells and perforations, and the remainder with questions relating to Tinsplate, Cans, Raw Products, Canning and Storage.

RELATIONSHIP BETWEEN HYDROGEN SWELLS AND PERFORATIONS

COMPARISON OF FRUITS

Quite a long period generally elapses between the formation of a hydrogen swell and perforation of the can, but any action which increases the dissolution of the iron in the baseplate tends to make for more rapid perforation. Certain fruits—bilberries are a notable example—readily cause perforation of the metal, but these are the exception rather than the rule, and in the present tests it was found that only about one to two per cent of the cans perforated before doming.

Some idea of the connection between hydrogen swells and perforations may be gained from the table on page 42, which shows the results recorded during the six seasons on the standard packs of each fruit used as “controls.” The figures show the percentage of hydrogen swells and perforations after storage for thirty-five weeks at 95° F., and, in spite of somewhat large fluctuations, display several points of interest. Blackcurrants, which readily form hydrogen swells, were amongst the least susceptible to perforation; loganberries also showed a noticeable resistance to perforation. These two fruits readily attack areas of exposed metal, and the resulting corrosion soon becomes visible; the attack on the tin coating is usually severe and often works its way under the lacquer at the seams or expansion rings. Sweet cherries, which are very prone to form hydrogen swells, were also slow to perforate in these tests. Here the attack was much less visible than in such fruits as blackcurrants and loganberries, and took place mainly in the seams. Morris (22) has pointed out that the dissolution of iron is very pronounced where cherries are concerned, and it is consequently a little

HYDROGEN SWELLS AND PERFORATIONS - EFFECT OF VARIOUS FRUITS

Stored 35 weeks at 95° F : Lacquered Cans

FRUIT	HYDROGEN SWELLS—per cent						PERFORATIONS—per cent					
	1930	1931	1932	1933	1934	1935	1930	1931	1932	1933	1934	1935
Gooseberries	2	72	3	35	—	10	0	8	0	3	—	0
Strawberries	55	86	86	70	100	90	20	2	24	15	75	35
Raspberries	56	59	84	40	75	75	36	28	30	15	52	13
Loganberries	60	91	70	96	58	50	12	5	3	12	15	20
Blackcurrants	84	95	100	97	98	70	14	3	0	9	2	0
Blackberries	28	57	54	54	0	10	5	0	17	18	0	5
Cherries (White)	65	100	93	100	93	83	3	95	12	18	13	5
Greengages	75	82	60	68	8	—	39	10	9	3	0	—
Pershire Plums	83	95	35	43	25	0	45	39	0	25	0	0
Victoria Plums	42	98	65	65	12	20	14	22	11	5	5	2
Damsons	22	98	23	30	35	8	0	0	0	3	0	0

difficult to account for the low percentage of perforations recorded in these tests.

The information given in this table does not treat each fruit at the same stage of its "hydrogen swell curve," and consequently does not enable a comparison to be made of the rate at which perforations succeed hydrogen swells in each class of fruit. When the percentage of perforations was recorded at the stage where 75 per cent of the cans had formed hydrogen swells the results were more uniform, the average figures being as follows :

Blackcurrants 3, white cherries 3, damsons 6, loganberries 11, golden plums 12, Victoria plums 12, strawberries 14, greengages 17, blackberries 26, and raspberries 28 per cent. Sufficient figures for gooseberries were not obtained, but the percentages, where noted, were low.

SITES OF PERFORATIONS

A record of the sites at which perforations occur is of value in showing the weak points in the can, but care should be taken to differentiate between the points at which perforations occur and those at which the maximum corrosion takes place. It is quite possible for severe corrosion to occur at the double right-angle bend of the lock of the side seam without producing a perforation of the can itself. Later on perforation may occur at one of the end seams, and the exposure of metal at this spot may easily be blamed for causing the hydrogen swell, while the fault really lay elsewhere. In such a case, protection of the metal on the side seam would be more important than protection of the end seam.

In the earlier years during which these tests were being carried out the manufacture of the open-top can was still to some extent in the experimental stage in this country, and the earlier tests at Campden revealed certain weak points which were made less vulnerable in subsequent years. The sites of perforations at the end of thirty-five weeks' storage at 95° F. are given in the following table, the seasonal figures all being based on the same proportions of each class of fruit.

SITES OF PERFORATIONS IN LACQUERED CANS

STORED 35 WEEKS AT 95° F.

Year	SEAMS		Expansion Rings	Body	Total Perforations	Total Hydrogen Swells
	End	Side				
	per cent	per cent	per cent	per cent	per cent	per cent
1930	2.4	1.3	0.3	14.7	18.7	57
1931	12.1	6.6	0.2	1.4	20.3	86
1932	5.8	0.5	2.9	1.5	10.7	67
1933	7.4	3.3	0.3	1.2	12.2	66
1934	15.6	0.1	0.5	0.6	16.8	50
1935	8.3	0.3	0.2	0.2	9.0	48

The percentage figures are reckoned on the total number of cans in the tests, and so show the absolute as well as the relative tendencies to perforate at various sites. The high figure for total perforations in 1934 was due to exceptionally heavy perforations in the strawberries and raspberries used that season ; the other fruits were all normal. The heavy losses from perforations on the body of the cans and the low percentage in the seams recorded in 1930 are worth noting; this may have been due to the quality of the tinplate used, but it is significant that extensive alterations in the can-making operations were made after that year. There appears to have been a slight but definite improvement in the cans during the last four years.

TINPLATE

VALUE OF CANNING TESTS

As the formation of hydrogen swells depends on the interaction between the can and its contents, the importance of studying the effect of the various chemical and physical factors connected with the tinplate may readily

be understood. The composition of the contents can only be modified to a small extent, but this is not the case with tinplate where there is still ample scope for improvement.

Unfortunately the methods used in tinplate manufacture do not enable each of the chemical and physical factors to be controlled separately for experimental purposes, consequently it is impossible to attach much value to the results of practical canning tests based on such material unless they can be analysed statistically. Laboratory methods are much more likely to yield useful results in preliminary studies, and some of these have been referred to in an earlier section of this publication. Practical tests can be of some value in connection with the large issues—such as the value of heavier tin coatings and the effect of “normalizing” the plate—and these latter points have been made the subject of canning tests referred to below.

POROSITY AND WEIGHT OF TIN COATINGS

The exposure of the steel baseplate in minute areas known as *pores*, or by means of scratches which penetrate through the tin coating, may lead to serious corrosion. Porosity naturally tends to decrease as the thickness of the tin layer increases, but it is always there to some extent in commercial tinplates. Its effect is less noticeable in lacquered than in plain cans, as the lacquer coating generally protects the plate at all points except in the seams and at places where the metal has been sharply bent in stamping out the ends. Irregularities in the tin surface may cause the first layer of lacquer to spread away from certain points, but continuity of covering is usually obtained by means of the second layer. Neither the porosity nor the weight of tin coating is likely to affect the state of the metal at points where severe mechanical strain has been set up, and it was noticed in these tests that the amount of steel exposed at these places did not vary greatly in the charcoal and coke plate cans used.

Tests were carried out in 1931, 1932 and 1933 on cans made from charcoal and coke plate; in each of the three seasons the former contained about thirty-two ounces and

the latter twenty-two to twenty-four ounces of tin per base box. In 1931, all four fruits tested gave much better results in the charcoal plate cans, the time of storage at 95° F. required to produce 25 per cent loss being as follows :

	<i>Charcoal</i>	<i>Coke</i>
Loganberries (lacquered cans)	48 weeks	17 weeks
White Cherries (plain cans)	29 „	6 „
Greengages (plain cans)	60 „	20 „
Golden Plums (plain cans)	90 „	57 „

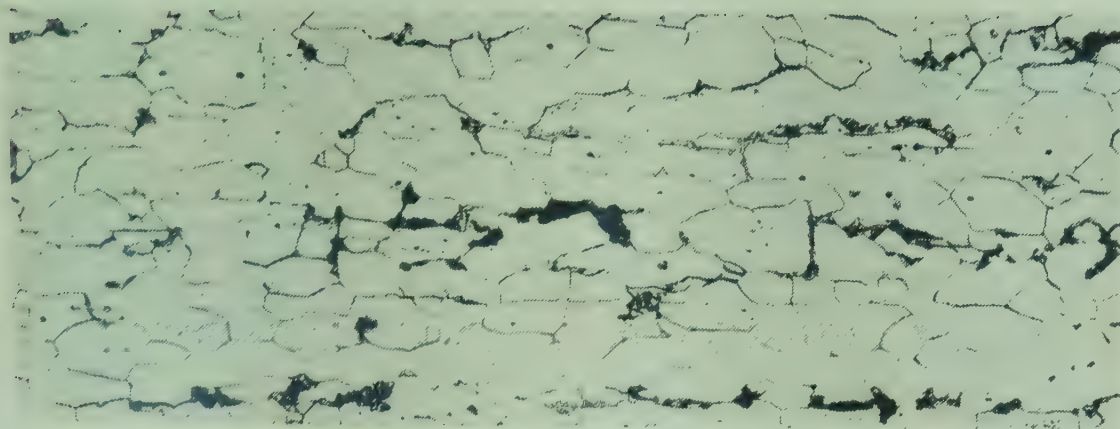
In 1932 the results were slightly in favour of the coke plate cans, while in 1933 the superiority of the coke plate was much more pronounced, the figures being as follows :

	<i>Charcoal</i>	<i>Coke</i>
Gooseberries (plain cans)	37 weeks	70 weeks
Loganberries (lacquered cans)	11 „	20 „
White Cherries (plain cans)	22 „	22 „
Greengages (plain cans)	22 „	48 „
Greengages (lacquered cans)	6 „	25 „
Golden Plums (plain cans)	26 „	69 „
Victoria Plums (lacquered cans)	7 „	23 „

The results appear to show fairly definitely that the heavier weight of tin coating did not, in itself, offer any great protection to the steel base. The discordant results in the three seasons' tests were evidently due to the operation of some other factor, probably connected with the composition of the baseplate ; but it is interesting to note in this connection that the phosphorus content was similar in both plates used in 1933, and so was evidently not the responsible factor. The fact that the differences between the two lots of plate under test were equally prominent in the lacquered and plain cans tends to confirm the suggestion that these were not due to variation in porosity.

Similar types of experiments—mainly on plain cans—conducted in America have also given very variable results with the balance generally in favour of the cans made from charcoal plate. In this country lacquered cans

PLATE I



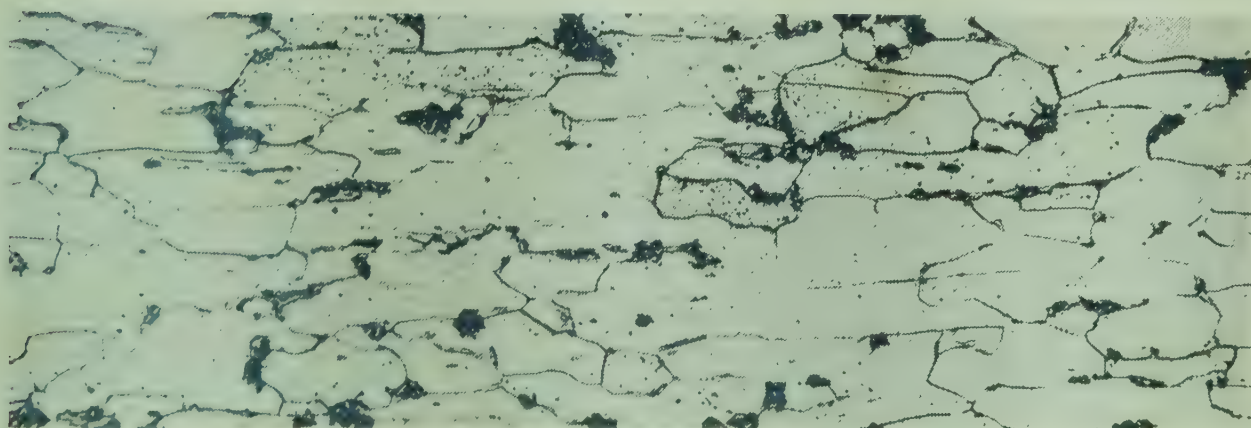
High Phosphorus (HP) Plate 1933

PLATE II



Low Phosphorus (LP) Plate 1933

PLATE III



Special (AL) Plate 1933

are chiefly used, and it seems doubtful whether a change to charcoal plate (either for the whole cans or only for the ends) would justify the extra cost.

CHEMICAL COMPOSITION OF BASEPLATE

There seems little doubt that the most important factors governing the formation of hydrogen in cans are to be found in the chemical constitution of the baseplate. This matter has been referred to at some length on page 28 and the importance of sulphur compounds in the steel emphasized. Certain desirable qualities in the steel are imparted by the so-called "impurities"—phosphorus compounds, for instance, are said to make easier the separation of the sheets after hot-rolling in the tinplate works. Unfortunately, some of these same impurities appear to accelerate corrosion, and in this connection, phosphorus compounds have at various times come under suspicion. Several canning tests were carried out to indicate broadly whether an excess of phosphorus in the steel increases the rate of corrosion.

An analysis of the steel is given below for three of the plates tested in 1933 :

Plate	Chemical Analysis of Steel (per cent.)						Tin Coating per base box	
	C	Si	S	P	Mn	Cu		
HP	0.12	0.010	0.069	0.165	0.41	0.109	32	ounces
LP	0.09	0.012	0.056	0.027	0.41	0.087	22	„
AL	0.11	—	0.096	0.062	0.42	—	22	„

The test in this case was between "high phosphorus" (HP) and "low phosphorus" (LP) plates. Unfortunately the former had also a high sulphur content—though the latter was also above the normal in this respect—and the carbon contents differed materially. The microphotographs (Plates I and II) also show that the non-metallic inclusions in the "HP" plate were very considerable. These various differences in composition made the test unreliable in regard to its main object—namely, to indicate the effect of phosphorus content on the rate of formation of hydrogen swells.

At the same time as this test was being carried out another sample of plate, referred to as "AL" was on trial. This plate had been tinned in a different type of tinpot, but the porosity appeared to be normal, and, as the plate was lacquered, the test became mainly a comparison between the corrodability of the baseplates.

The interesting point about this plate was that its composition and structure strongly resembled the "HP" plate, except that the position in regard to sulphur and phosphorus was more or less reversed in the two plates. The results of the canning trials on the three lots of cans were as follows :

HIGH AND LOW PHOSPHORUS AND "AL"
PLATES (1933)
STORED 95° F. : PERIODS TO REACH 25 PER CENT LOSS

Fruit	High Phosphorus (HP)	Low Phosphorus (LP)	Special Plate (AL)
Loganberries	weeks 11½	weeks 40	weeks 10½
Greengages	9½	63	7
Victoria Plums	9½	91	8½

These results are not conclusive as they must have been influenced by more factors than one. The difference in sulphur content probably had a greater effect than the difference in phosphorus content, but it should be noted that very good results were obtained with the "LP" plate in which the sulphur content was high and the phosphorus content low. It is interesting to note that laboratory tests on detinned strips of the two plates "LP" and "HP" showed that the latter corroded two and a half times more rapidly than the former.

An attempt was made in the following year to produce batches of mild steel sheets of low phosphorus content on a full commercial scale. Three "heats" of steel were pre-

pared, but the phosphorus content could not be reduced below 0.040 per cent; there was a high percentage of “wasters” among the plates, and consequently variable factors other than phosphorus were probably introduced. The composition of two of the test plates is given below together with that of the standard plate used for the “controls.”

Plate	Chemical Analysis of Steel				Tin Coating	
	C	S	P	Mn		
Heat B	0.09	0.058	0.041	0.36	per cent	27 ounces
Heat C	0.09	0.076	0.043	0.39	„	27 „
“Control”	0.10	0.065	0.055	0.38	„	28 „

The phosphorus content of the test cans was only slightly less than that of the “controls,” but it was noticeable that the sulphur content in Heat C was high. The microphotographs (Plates IV and V) also show that Heat C contained a greater amount of non-metallic inclusions; both these factors are likely to increase corrosion. The results of the canning trials are given below :

LOW PHOSPHORUS PLATES (1934)
 STORED AT 95° F. : PERIODS TO REACH 25 PER CENT LOSS

Fruit	Can	Heat A	Heat B	Heat C	Control
		weeks	weeks	weeks	weeks
Loganberries	A2	24	30	31	26
Greengages	A2	36	53	30	42
Golden Plums	A2	39	70	30	33
„	A2½	38	66	52	26

It will be seen that neither Heat A nor Heat C appeared to show any improvement on the “control”; Heat B, however, was distinctly better. It seems improbable that this difference was due to the phosphorus content, though it may have been caused to some extent by the amount of sulphur in the steel. The fact that the phosphorus content,

taken as a single factor, seems unlikely to be one of the main influences regulating corrosion may be further deduced from the results of the tests on the low phosphorous "strip plate" recorded below. In spite of the doubts still remaining on the subject it can be said that the tests in 1933 and 1934 have shown two points fairly clearly—(1) that variation in composition of the steel baseplate can account for very great differences in the rate of corrosion and hydrogen formation, and (2) that the method of testing by means of canning trials is unsatisfactory (unless applied statistically on a large-scale run) for determining the effect of single factors connected with the chemical composition of the steel base.

STRIP PLATE

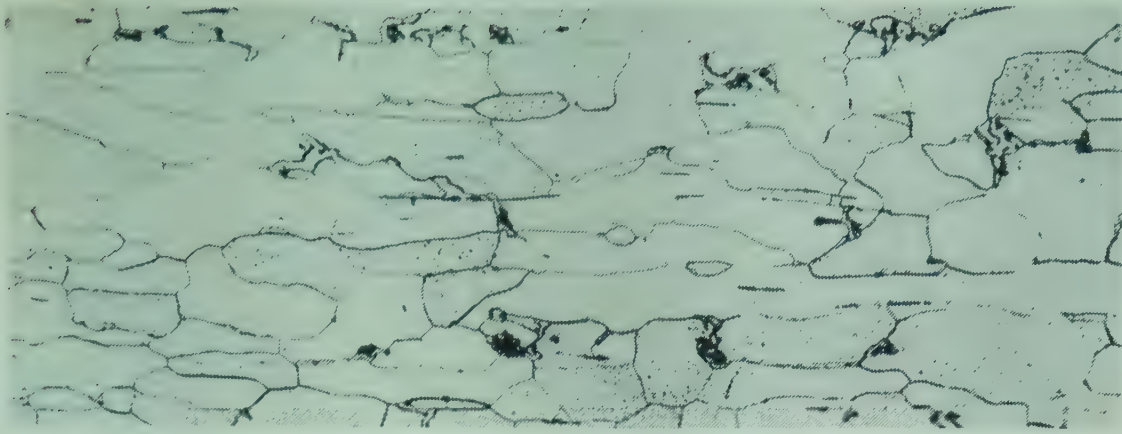
Certain improvements can be effected in the quality of tinplate by reducing the percentage of impurities present in the steel. To bring these about extensive alterations in the methods used in the tinplate works are necessary, and the rolling of each steel bar into a single strip is now carried out as a commercial process in a few mills in various parts of the world.

In 1934 cans prepared from two lots of strip plate were included in the canning trials. In one lot the cans were made in a United States factory, and in the other they were made in England; in both cases the plate used came from an American strip mill. The chemical composition is shown below, and the microstructure in Plate VII.

Cans Made	Chemical Analysis of Steel				Tin Coating
	C	S	P	Mn	
U.S.A.	0.085	0.025	0.015	0.39	per cent 22 ounces
England	0.080	0.035	0.018	0.40	„ 18 „
Control	0.100	0.065	0.055	0.38	„ 28 „

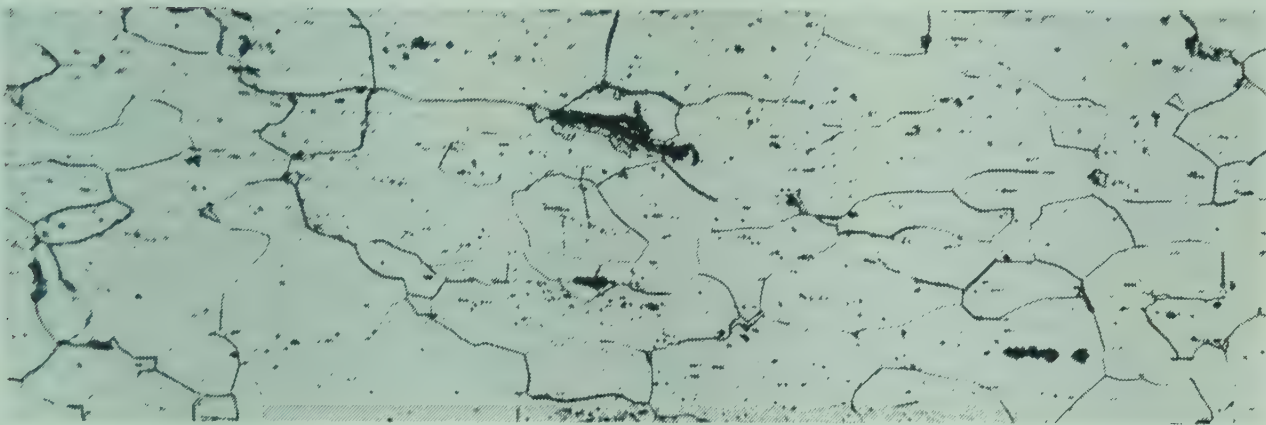
The results of the canning trials were as follows :

PLATE IV



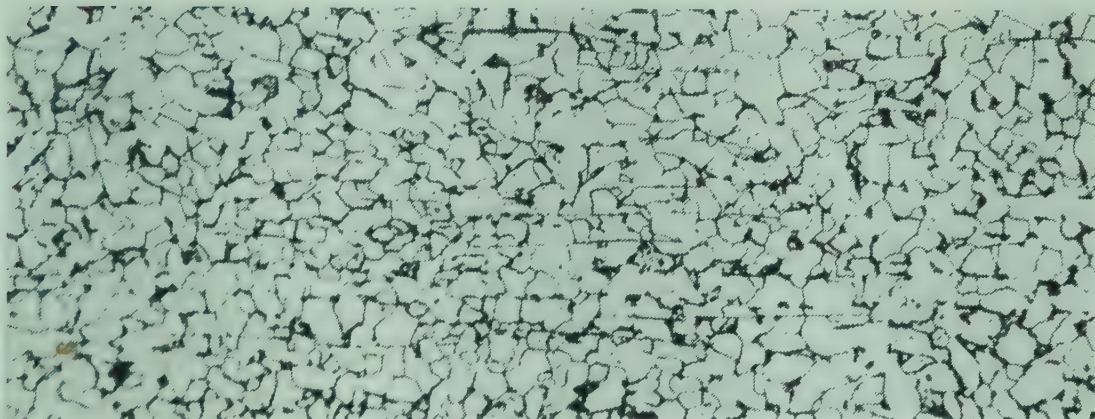
Low Phosphorus Plate — Heat B. 1934

PLATE V



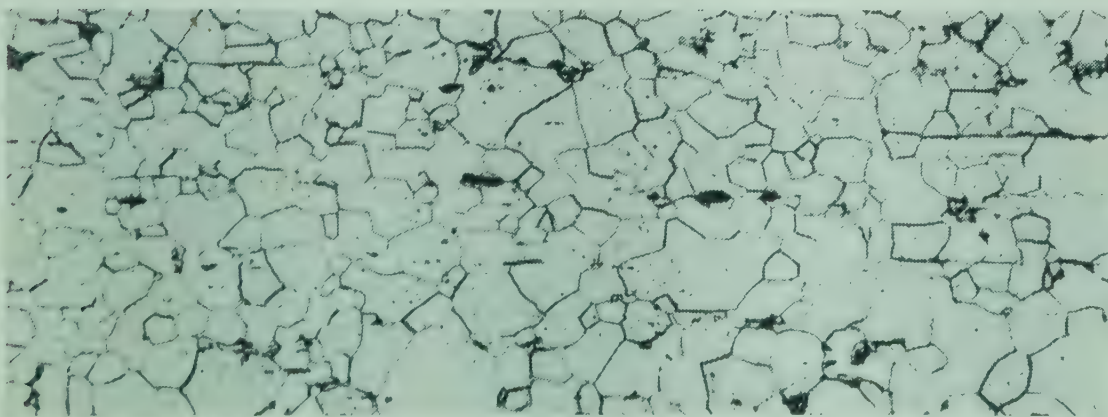
Low Phosphorus Plate — Heat C. 1934

PLATE VI



Low Phosphorus Plate — Heat C. Normalized 1934

PLATE VII



U.S.A. Strip Plate 1934

STRIP PLATE CANS (1934)

STORED AT 95° F. : PERIODS TO REACH 25 PER CENT LOSS

Fruit	Strip Plate (U.S.A.)	Strip Plate (England)	Control
	weeks	weeks	weeks
Loganberries	19	31	26
Greengages	—	56	42
Golden Plums	—	62	33

It will be noted that the strip plate cans made up in England were rather better than the controls, but that the cans obtained direct from America were decidedly poorer. It is understood that good results have been obtained with strip plate in canning trials carried out in the United States, but the tests noted above do not show as marked an improvement as might have been expected from the use of a steel possessing such low carbon, sulphur and phosphorus contents. It appears that some other important factor still undiscovered contributed in producing these results.

PHYSICAL STRUCTURE

Mention has already been made of the importance of the distribution of impurities throughout the steel bars used for making tinplate. This factor has not been studied in these canning tests, as the difficulty of obtaining uniform samples of plate would make such tests of little value.

A point of considerable importance worth examining—and one which should yield reasonably reliable results in canning trials—is the effect of the crystal size of the iron in the steel baseplate. This can be altered by varying the rate of cooling of the metal, but a more radical change can be brought about by raising the temperature of annealing above a certain point. This treatment is known as “normalizing” and produces a finer-grained crystal structure.

As the chief points at which corrosion takes place are

those where the metal has suffered mechanical strain in die-stamping of the ends or formation of the side seams it might be thought that large crystals would penetrate the surface layers at the lines of fracture more easily than smaller crystals. On the other hand small crystals have a greater total area of boundary than large, and so offer better facilities for the release of any hydrogen that may form ; they thus might accelerate corrosion. The essential point in any comparative tests is that the steels used should be of the same chemical composition, and vary only in their crystal size. This was aimed at in the "phosphorus" tests of 1934, where the three heats of steel mentioned previously were annealed in two batches, one at the ordinary temperature and one at a temperature sufficiently high to normalize the metal. Unfortunately the methods used in this test produced tinplate of variable quality with a high percentage of "wasters" ; the result was that the canning trials showed a lack of uniformity in the rate of formation of hydrogen swells.

EFFECT OF NORMALIZING (1934)
STORED AT 95° F. : PERIODS TO REACH 25 PER CENT LOSS

Fruit	Can	Crystal Structure	Heat A	Heat B	Heat C
			weeks	weeks	weeks
Greengages	A2	Ordinary	36½	53	30
„	A2	Normalized	34½	36	36
Golden Plums	A2	Ordinary	39	70	30
„	A2	Normalized	42	43	37
Golden Plums	A2½	Ordinary	38	66	52
„	A2½	Normalized	35	40½	14½

In spite of the variable results in several of the tests it will be noted that in Heat B (which was the best heat of the plates which had received the standard annealing) the normalizing seemed to reduce the service-life of the cans very considerably. In the $A_{2\frac{1}{2}}$ cans all three heats gave poorer results with the normalized plate.

An interesting confirmation of these results was obtained when corrosion tests were carried out on strips of detinned metal from each lot of tinplate. The strips of metal three inches by one inch were immersed in a standard corroding medium and held for three days at 25°C . The average loss in weight of the samples tested is given below :

			<i>Ordinary</i>	<i>Normalized</i>
Heat A	0.1108 grm.	0.1345 grm.
Heat B	0.1040 „	0.1326 „
Heat C	0.1146 „	0.1268 „

The results of the practical canning test and the corrosion experiment both tend to indicate that normalizing increases the rate of attack on the steel base.

CONCLUSIONS—AND RESEARCHES IN PROGRESS

Practical canning trials such as those described above are unsuitable for determining the effect of single factors connected with the chemical composition of the steel baseplate, and can only give a general guidance to the causes of accelerated corrosion. Phosphorus compounds appear to increase the rate of corrosion, but to what extent is unknown. Sulphur compounds have probably a more marked accelerating effect. Normalizing seems to bring about an increase in the rate of formation of hydrogen swells.

Various practical canning trials are still in hand at Campden and proposals for the coming season include large scale tests in collaboration with the International Tin Research and Development Council on cans made from a large random sample of commercial tinplates of different chemical composition. The actual canning trials in these proposed experiments will be conducted at

Campden and at the Low Temperature Research Station at Cambridge, while the chemical compositions will be determined at the Metallurgical Laboratories at Cambridge. The results will be analysed statistically to indicate the significance of the various factors. Only by a method such as this can the effect of single factors, *acting in the presence of all other factors*, be studied.

CANS AND CAN-MAKING

MECHANICAL ASPECTS OF DOMING

The formation of a hydrogen swell is essentially a mechanical process—a forcing out of the ends as a result of pressure developed inside the can—and a knowledge of the reaction of the can to pressure is consequently of importance in the present study.

It is necessary first of all to define the word “headspace” which will be taken to mean the gas space at the top of the can after processing and cooling, and with the ends drawn in under vacuum. The A2 can has a capacity of about 580 cubic centimetres and each one-eighth of an inch of headspace corresponds to roughly seventeen cubic centimetres; a good normal headspace is about three-sixteenths of an inch in depth, or about twenty-five cubic centimetres in volume.

It is the usual practice to exhaust the cans until the central temperature is about 170° F.; this does not mean that the whole of the contents are at this temperature, for the inner parts of the fruits and the surface layer of the whole contents are cooler, while the outer layers in contact with the body and base of the can are hotter. In the case of large fruits, such as plums, through which heat penetrates relatively slowly, the variation in temperature throughout the contents is quite considerable.

If we take the case of cans of fruit with the contents at an average temperature of 170° F., passing under displacement toppers adjusted to enter the cans to a depth of one-quarter of an inch, then, the lid occupying about one-eighth of an inch, there will be roughly one-eighth of an inch of gas space left at the time of closure. After processing the cooling will increase this gas space through the

contraction of the contents; the contraction from 170° F. to 55° F. would amount to about fifteen cubic centimetres if the contents consisted entirely of syrup of the usual strength, but it is generally less than this amount in practice. The contraction of the gases in the headspace produces a partial vacuum which tends to remove gases from solution in the syrup; these gases were originally present inside the fruits or were generated by the action of the acid fruit juices on the substances producing temporary hardness in the water. The drop in pressure also draws the ends of the cans inwards, thus reducing the headspace by two or three cubic centimetres. The final result of these processes is to produce a vacuum of about twelve to fifteen inches in most cases, and a headspace of about twenty-five cubic centimetres.

Corrosion commences almost immediately the cans are closed, the first sign of this action being the disappearance of the traces of oxygen entrapped in the headspace. In the case of plain cans the oxygen disappears in the course of a few days, but in lacquered cans it does not go completely for several weeks. Horner (13) has shown that the removal of oxygen produces quite an appreciable increase in the vacuum. After this last stage is reached hydrogen starts to form, and it may be useful to follow the physical processes which take place within the can from this point until it becomes a hydrogen swell.

The mechanical characteristics of individual cans vary considerably, but the A2 can at present in general use has been found on the average to behave as follows: as the vacuum in the can falls from fifteen to ten inches the ends move outwards so that the volume of the headspace increases by about one cubic centimetre; there is a further increase of roughly the same amount between ten and five inches vacuum, and again between five inches and zero vacuum. As a positive pressure develops the ends continue their outward movement until the volume of the can has increased by about four and a half cubic centimetres from the "zero vacuum" position; at this point, which is reached when the internal pressure has risen to about seven and a half lbs. per square inch, one end springs out-

wards. This is an important stage, as it is here that the can becomes a hydrogen swell. This doming of one end increases the volume by about seven and a half cubic centimetres, and thus causes a temporary reduction in pressure, but the latter increases as more hydrogen is formed, and, at about eight lbs. pressure, the second end domes. The increase in volume beyond the "zero vacuum" stage is now about twenty-one to twenty-two cubic centimetres.

With these figures it is possible to indicate the volume of hydrogen required to produce doming under certain specified conditions, provided always that the headspace gases remain in the can in the gaseous state. If this were the case the ratios of the volumes in the examples shown below would give a general idea of the relative rates at which hydrogen swells would be likely to form—the ratio being inversely proportional to the volumes of hydrogen. In practice, however, more hydrogen than is indicated will be required in all cases, as the increased pressure will force some of the headspace gases into solution and there may be an escape of hydrogen by diffusion through the metal. The magnitude of this combined effect is unknown, but is probably not very great at the relatively low predomining pressures ; it will tend to diminish the disparities shown in the examples. It might be noted also that the rates of corrosion will not be quite the same in each of the pairs in the first two examples, but the effect in this case will be to emphasize the differences and thus lay further stress on the importance of an adequate headspace and a high initial vacuum.

<u>Factor Varied</u>	<u>Extent of Variation</u>		<u>Vol. of H₂ Required</u>	
	A	B	A	B
(1) Headspace	30 c.c.	10 c.c.	41½ c.c.	21½ c.c.
(2) Vacuum	15 in.	5 in.	41½	28½
(3) External Temperature	55° F.	80° F.	41½	37
(4) External Pressure	30 in.	25 in.	41½	35

The effect of varying four factors—headspace, vacuum, external temperature, and external (i.e. atmospheric) pressure—is shown in the above table. The standard conditions (marked A in the table) from which the comparisons are made are—30 c.c. headspace; 15 in. vacuum;

constant temperature of 55°F. ; and atmospheric pressure of 30 in. of mercury. The volumes of hydrogen required are all referred to this temperature and pressure.

It should be noted that the mere removal of a can to a warmer store (Example 3) brings it nearer to the doming state; this is quite apart from the effect of the higher temperature on the *rate* of corrosion. In this example it has been assumed that the rise in temperature brought about an increase of 2 c.c. in the volume of the contents.

The fourth example is given in order to show the effect of low atmospheric pressures, and in this respect it may be mentioned that such conditions tend to occur at high altitudes.

The pressures required to produce doming are largely governed by the contour of the expansion rings, though they are naturally influenced as well by the diameter of the ends and the gauge of the plate. The object of the expansion rings is to allow the can to increase in volume during processing, but they must be so constructed that they will cause the ends to be drawn in on cooling. Too rigid a structure is liable to strain the seams during processing and may make it necessary to press the ends in by hand after the cans are cool.

The figures given above refer to the standard A2 can at present in general use. An alteration in the gauge of plate might enable cans to be made with a higher doming pressure, but the advantage thus gained would probably be more than offset by counteracting disadvantages—both economic and technical. As things are, the doming pressure is reasonably high and canners have it in their power to see that it is not reached too soon by giving proper attention to the efficiency of the exhaust process and the production of an adequate headspace.

The relationships between pressure and volume in the A2 can were obtained by means of the apparatus designed for this purpose at Campden and described in a paper by Adam and Stanworth (2).

DAMAGE TO TIN COATING

The processes of can-making are such that the tinplate

has to be bent sharply at the side-seams and flanges, while the metal of the ends has to suffer the strains of die-stamping. The tin coating is not sufficiently elastic to withstand such severe treatment without fracturing, and both the surface layer of tin and the intermediate layer of tin-iron compound are affected. It is at these fractures—where the steel baseplate is exposed—that most of the corrosion takes place. Unfortunately, it is impossible entirely to eliminate mechanical damage of this sort, but it can be kept to a minimum by using dies which are not too sharp. Expansion rings are necessary for the reasons given in the previous paragraph, and are seldom responsible for heavy corrosion. The greatest trouble comes from the double right-angle bend of the side-seam, and the single right-angle bend on the ends close to the end-seam. Even in the best types of lacquered cans these areas are not completely covered, though they are generally the only parts of the metallic surface which are not well protected. Lacquer surfaces vary in their elasticity, but even the best break down when bent at such large angles of such small curvature.

The chief practical problem connected with hydrogen swells is therefore to discover some method of lacquering which will offer complete protection to these damaged areas, just as the chief fundamental problem is to find a slow-corroding steel baseplate.

TYPES OF CANS

As far as the effect of the size of the cans is concerned little experimental evidence can be quoted, as the tests at Campden were confined almost entirely to the A2 size. It is worth noting, however, that—other factors being equal—the smaller the diameter of the can the higher is the pressure required to produce doming. This would tend to indicate that A10 and A2½ cans should form hydrogen swells more readily than E1 cans, but other points have to be taken into consideration, notably that the smaller cans have a larger corroding area of metal in proportion to their volume, and that the curvatures being sharper, there is a greater chance of damaging the metal in stamping out the ends of the smaller sizes.

In 1933 tests were made on cans which were similar in regard to the contour of the ends save that in one lot the central panels (or “strengthening rings”) were omitted. The absence of strengthening rings probably reduced the rate of corrosion slightly, but the pressure required to produce doming was lessened, and the cans were found to form hydrogen swells rather more easily. The following figures—based on the average results of tests on seven different lacquers—show the normal type of can to be the better.

EFFECT OF OMITTING STRENGTHENING RINGS

STORED AT 95° F.: PERIODS TO REACH 15, 25, AND 50 PER CENT LOSS

Fruit	Normal			No Strengthening Rings		
	15 per cent	25 per cent	50 per cent	15 per cent	25 per cent	50 per cent
	weeks	weeks	weeks	weeks	weeks	weeks
Logan-berries	17	19½	24	14½	17½	25
Black-currants	9½	11½	15½	9	11	15
Victoria Plums	20	24½	30	13	16	22

LACQUERS AND LACQUERING

Lacquered cans have many advantages over plain cans, but they unfortunately form hydrogen swells more readily. The theoretical aspects of this question have been dealt with on page 28 and may be summed up in the statement that the type of corrosion in a plain can favours the relatively slow process of dissolution of tin and retards the attack on such areas of steel as are exposed, while the corrosion in a lacquered can tends to concentrate on the

steel which dissolves rapidly in the absence of the full protection afforded by tin. The fact that lacquered cans are less satisfactory than unlacquered in this respect is well known, and has been demonstrated on many occasions, but the results of tests at Campden included in the following table show certain additional points of interest.

EFFECT OF LACQUERING
STORED AT 95° F.

Fruit	Cans	Periods to Reach Loss of		
		15 per cent	25 per cent	50 per cent
		weeks	weeks	weeks
Gooseberries	Lacq'd	17	24	29
„	Plain	40	46	60
White Cherries	Lacq'd	17	18	21
„	Plain	17	19	25
Greengages	Lacq'd	19	23	30
„	Plain	30	34	42
Golden Plums	Lacq'd	18	24	31
„	Plain	52	61	77

The figures for white cherries, greengages and golden plums are all averages of tests carried out during four or five seasons; the figures for gooseberries were from only one sample of fruit—a sample which was exceptionally active in promoting hydrogen swells. The results obtained for white cherries are worth noting, as in all four seasons the lacquered cans gave almost as good results as the plain; this is particularly interesting in view of the

general abnormal behaviour of this weakly-acid fruit. With greengages the advantage of using plain cans was well-marked in all the trials carried out; with golden plums the advantage was still more pronounced in all cases.

In 1933 and 1934 about twenty different lacquers were tested in an attempt to ascertain whether some—by reason of greater elasticity—offered more protection than others to the areas where the tin coating had been fractured. Most of these lacquers were prepared from natural copal gums, but a few were made from synthetic resins. In all cases the normal method of application was used, the stencilled plates being stoved before cutting and forming into cans. Some lacquers gave better results than others as regards freedom from visible attack at the seams and expansion rings or along scratches in the bodies, but most of these fared worse than the rest in regard to hydrogen swells. The higher proportion of tin in solution in the contents of the cans which showed obvious imperfections was probably the cause of the fewer losses from hydrogen swells in these cases. For the same reason the single lacquered cans showed fewer losses from hydrogen swells than the double lacquered, though they were distinctly less satisfactory in other respects. These tests indicated that the problem of hydrogen swells was not likely to be solved merely by altering the type of lacquer used. Tests on the addition of inhibitors to the varnish before stoving were rejected as it was felt that the practice was likely to be an undesirable one; the inhibitors would have to go into solution in the contents to become fully effective and most metallic substances are thus ruled out. Organic inhibitors would have to withstand the high stoving temperatures without decomposing.

PROTECTION OF SEAMS

Kohman has pointed out that extensive corrosion occurs inside the end-seams where the seaming rollers tend to produce a series of minute but sharp puckers in the metal. These puckers are due to the hardness of the metal, the tangential movement of the first operation roller tending

to make the seam polygonal rather than circular; the second operation roller cannot smooth out these puckers. At the sharp points produced in this way the tin coating is fractured and the steel base exposed, thus forming ideal sites for corrosion.

In spite of these findings the general conclusions based on the Campden trials have been that there is much less corrosion inside the end seams than at the right-angle bend of the lids immediately adjacent. The trouble, therefore, arises not as a result of the seaming operation, but on account of the damage done to the tin coating and lacquer surface in stamping out the ends. This distinction is important from a practical standpoint when it comes to the question of finding some means of protecting the areas of exposed metal. If the seaming operation had been the chief cause of trouble then the only remedy would have been for the can-maker to spray lacquer the cans after they had been made up. If the ends are chiefly to blame, however, protection should be gained by spray lacquering them before they are spun on; this presents a much less formidable problem. The side seams are also sites of lively corrosion and must be protected by spray lacquering, by painting with a quick-drying lacquer, or by some process producing similar results.

In view of the conclusions arrived at it was decided to make a test of cans in which the ends had been spray lacquered after stamping out, and the bodies had been spray lacquered at the stage when they were open-ended cylinders. Another set of cans, taken from the same lot as the "controls" used for this test, were painted with an air-drying lacquer round the base seam and along the side seam. The results of the trials carried out in 1934 and 1935 are recorded in the following table.

SPRAY LACQUERING AND PROTECTION OF SEAMS

STORED AT 95° F.

Fruit	Year	Test	Periods to Reach Loss of	
			15 per cent	25 per cent
			weeks	weeks
Loganberries	1934	Spray Lacquer	77	87
	"	Painted Seams	78	82
	"	Control	22	26
Blackcurrants	1934	Painted Seams	43	46
	"	Control	14	15½
Greengages	1934	Spray Lacquer	86	90
	"	Control	36	42
Golden Plums	1934	Painted Seams	69	74
	"	Control	30	33
Loganberries	1935	Spray Lacquer	*	*
	"	Painted Seams	73	*
	"	Control	23½	24½
Gooseberries	1935	Spray Lacquer	*	*
	"	Painted Seams	*	*
	"	Control	36	38
White Cherries	1935	Spray Lacquer	68	*
	"	Control	21	24
Blackcurrants	1935	Spray Lacquer	52	57
	"	Painted Seams	36	38
	"	Control	24	26
Golden Plums	1935	Spray Lacquer	*	*
	"	Painted Seams	*	*
	"	Control	65	72

The items marked with an asterisk are tests in which the losses were below 15 per cent. at the time of publication of the monograph. The percentage losses in each of the blocks of the 1935 tests after 75 weeks' storage were as follows: loganberries 0, 15, and 100; gooseberries 5, 10, and 100; white cherries 24 and 100; plums 0, 0, and 40.

Both methods of protecting the seams appear to have been highly successful, as the life of the cans by both treatments was lengthened nearly threefold. The painting of the end-seams covered up any faults produced during the seaming operation, while these faults remained exposed in the case of the spray lacquered cans; on the other hand, the bodies were more fully protected in the latter test. Further batches of cans were packed in 1936 to determine which of the two danger spots—the end seam or side-seam—contributed more to the ultimate losses from hydrogen swells. The results are not yet available.

These experiments show fairly definitely that the development of some method of protecting the exposed areas of metal at the side seam and on the ends should greatly reduce the present trouble from hydrogen swells. This improvement would also be reflected in the storage properties of the canned product, the natural colour and full flavour of the fruits and the clarity of the syrup being preserved for a much longer period by these means. The chief difficulty in the way of immediate adoption of the protected seam on a commercial scale is to discover a practical method of applying the protective coating of lacquer in the can-making factory; this, however, is a problem for the can-maker to solve, and has already been given serious attention.

Any such developments will have to be tested on a semi-commercial scale to begin with, and alteration of existing plant can only come about when these preliminary large-scale experiments have been concluded. At the moment it appears that the hydrogen swell problem can best be solved along these lines until some radical change can be made in the corrodability of commercial grades of tinplate.

RAW PRODUCTS

COMPARISON OF FRUITS

The chemical composition of fruits varies greatly, and shows these differences very markedly in the rate at which they promote the formation of hydrogen swells. Acidity, as measured by the pH value, is only one factor in this

connection; substances capable of removing dissolved tin from the solution tend to increase the rate of corrosion; physico-chemical differences are important as they affect adsorbing surfaces, while individual fruits probably contain accelerators or inhibitors of corrosion and may contain colouring matter capable of acting in a similar manner to oxidizing agents, thus causing depolarization. In view of this wide variation in chemical properties it is not surprising to find that fruit juices differ greatly in the rate at which they bring about corrosion of the tin-iron couple. This difference is not only noticeable as between one type of fruit and another, but also between varieties of the same fruit, and even between the same varieties grown or picked under different conditions. The list given in the table below shows the average rates of corrosion of the "controls" packed during each of the six seasons between 1930 and 1935.

TYPES OF FRUITS—AVERAGE RATES
OF LOSSES
STORED AT 95° F.: DOUBLE LACQUERED CANS

Fruit	Periods to Reach Loss of			
	First Loss	15 per cent	25 per cent	50 per cent
	weeks	weeks	weeks	weeks
Blackcurrants	13	16	18	29
WhiteCherries	14	17	18	21
Pershire				
Plums	11	18	24	31
Greengages	16	19	23	30
Victoria				
Plums	14	21	23	30
Raspberries	15	21	23	32
Strawberries	17	21	24	28
Loganberries	17	22	25	32
Damsons	20	26	31	43
Blackberries	23	30	34	38
Gooseberries	24	38	44	58

The order in which the fruits should be placed is best taken from the storage periods given for 15 and 25 per cent losses, but it should be mentioned that most of these figures were obtained from only six to eight tests in which the results were often very variable. General observation would probably place white cherries (canned without added acid) as the worst fruit, followed by all classes of plums with the exception of damsons. Blackcurrants would come next, and then the remaining fruits as shown in the list. The slightly higher position occupied by plums in commercially packed cans is probably due to over-filling with syrup and will be referred to later.

It was noted that the white cherries showed very great variations between different samples of fruit, and that this was not entirely a question of pH value. Greengages, Pershore plums and Victoria plums were even more variable, while the seasonal results obtained with damsons and cultivated blackberries were fairly uniform.

EFFECT OF RIPENESS STORED AT 95° F.: PERIOD TO REACH 15 AND 25 PER CENT Loss

Fruit	Firm Ripe		Under Ripe	
	15 per cent	25 per cent	15 per cent	25 per cent
	weeks	weeks	weeks	weeks
Strawberries	17	19	17½	20
Victoria Plums (1)	13½	15	16½	18
„ (2)	33	41	41	49
Pershore Plums	44	56	63	77

EFFECT OF RIPENESS

Some fruits, such as Pershore plums, are canned at various stages of ripeness, and it is of interest to know

whether a controllable factor of this type has any pronounced effect on the rate of corrosion. Plums and strawberries were tested, the firm-ripe and under-ripe fruits being selected from the same consignments and canned at the same time. The Pershore plums were packed in plain cans, the strawberries and Victoria plums in lacquered cans.

It will be seen from the table that in all cases the tendency to promote hydrogen swells increased slightly as the fruit ripened. It is improbable that this was entirely due to the increase in the pH value, which did not exceed 0.15 in any of the tests.

HOLDING FRUIT BEFORE CANNING

STORED AT 95° F.: PERIODS TO REACH 15 AND 25 PER CENT LOSS

Fruit	Controls		Held Fruit	
	15 per cent	25 per cent	15 per cent	25 per cent
	weeks	weeks	weeks	weeks
Loganberries	22	26	24	27
Greengages	37	42	38	42
Pershore Plums	61	73	69	74

HOLDING FRUIT BEFORE CANNING

It is sometimes found necessary to hold fruits in store over night before canning. Plums may be held for several days between picking and canning, as the fruit has often to be sent long distances by rail. Dry unbruised fruit can remain alive and in good condition for a considerable period after it has been picked, provided it is placed in a cool store with a steady current of air passing over it. The loganberries in this test were held under such conditions for four days and the greengages and plums for three days

after selecting the fruit at random from the consignments from which the "controls" were packed. The test was thus a rigorous one as far as loganberries were concerned, though the holding period was quite normal in the case of the greengages and plums. The Pershore plums were packed in plain cans, the loganberries and greengages in lacquered cans.

The results show that the ripening changes occurring in fruits stored under good conditions for several days between picking and canning do not appear to influence the rate of corrosion appreciably; if anything, the rate seems to be reduced slightly.

STRIGS IN BLACKCURRANTS

This fruit attacks the cans severely and generally produces hydrogen swells rapidly. As corrosion may be accelerated or retarded by minute traces of certain natural chemical substances in the fruit it was felt that the stalks of blackcurrants—which are sometimes imperfectly removed—might have some influence on the rate of corrosion. A sample of blackcurrants was taken and a portion for the "controls" was strigged very thoroughly; in the remainder about one-half of the stalks were allowed to remain on the currants. The results showed that the unstrigged fruits actually gave an appreciably lower rate of corrosion than those which had been well strigged.

TYPE OF SUGAR USED

Morris and Bryan (19), after experimenting on steel strips immersed in acidified solutions of various sugars, pointed out that cane sugar brought about more rapid corrosion than beet sugar. The former appeared in some cases to contain an active accelerator of corrosion, while the latter almost always contained an inhibitor. Substances such as these, which materially alter the rate of corrosion, can only be present in minute quantities, and their action is such that it might quite easily be interfered with in a highly complex corroding medium such as that found in canned fruits. For that reason it was decided to

carry out practical canning trials on this subject at Campden. The results of the first two years' trials were indecisive, being sometimes in favour of one type of sugar and sometimes of the other, but it was found that most of these sugars did not give widely different results when tested under the standard laboratory conditions used at Cambridge. One sample, however—a batch of cane sugar kindly procured by Morris and showing a loss of weight of 0.0651 gram in the standard laboratory corrosion test—was compared with a sample of beet sugar which had only shown a loss of weight of 0.0288 gram under similar laboratory conditions. Greengages were packed in this canning trial at Campden and reached 15 and 25 per cent losses in nine and fifteen weeks respectively with the cane sugar, and in fifteen and thirty-five weeks with the beet sugar. These findings, which tended to indicate that the accelerators and inhibitors present in commercial sugars markedly influenced the rate of formation of hydrogen swells, were not confirmed in tests made in the following years.

In 1932 three samples of sugar were tested for rate of corrosion under laboratory conditions:

(a) Cane sugar (refined)—loss in weight	0.0949 g.
(b) Beet sugar (refined)—	0.0288 g.
(c) Cane sugar (unrefined)—	0.0277 g.

The canning tests at Campden gave the results shown in the next table.

The results are interesting for they show that, despite the wide differences in the corrosion rates recorded in the laboratory tests on steel strips, the production of hydrogen swells was fairly uniform for the three sugars. Only in the case of white cherries did the low-corroding beet sugar give better results than the high-corroding sample of cane sugar, but the improved result was not repeated in the sample of unrefined cane sugar. Further tests, to be referred to later, indicate that the action of inhibitors and accelerators in canned cherries is highly complicated.

EFFECT OF TYPES OF SUGAR

STORED AT 95° F.: PERIODS TO REACH 15 AND 25 PER CENT LOSS

Fruit	Cane (Refined)		Beet (Refined)		Cane (Unrefined)	
	15 per cent	25 per cent	15 per cent	25 per cent	15 per cent	25 per cent
	weeks	weeks	weeks	weeks	weeks	weeks
Straw- berries	19	21	—	—	18	19
Logan- berries	28	30	28	31	28	32
White Cherries	39	41	56	60	39	40
Pershire Plums	47	55	45	55	—	—

In the above tests the strawberries and loganberries were packed in lacquered cans, the cherries and plums in plain cans. The syrup used for the cherries contained 0.5 per cent of citric acid. The pH values of the canned fruits were 3.45, 2.95, 3.46 and 3.07 respectively.

It is interesting to note in this connection that Morris and Bryan (20) obtained better results with beet sugar than with cane in practical canning tests.

It will be seen that the accelerators and inhibitors of corrosion contained in cane and beet sugars do not necessarily act very strongly in the presence of fruits, but that there appears to be a distinct advantage gained in some cases by using beet sugar. Cannerymen would be well advised to take the precaution of using this type of sugar, though there is very little evidence in these tests to show that it can be a factor of major importance in the problem of hydrogen swells.

One other type of sugar has recently been tested at

Campden, namely a liquid cane sugar such as is used commercially in some jam factories. This sugar showed a much higher percentage of direct perforations than normal cane sugar and the total losses were decidedly more severe. Samples of liquid sugar will undoubtedly vary according to the nature of the sample of cane sugar from which they are prepared, but it is quite possible that these results indicate an actual change which is brought about during the process of preparation and storage.

ADDITION OF ACID

As the rate of formation of hydrogen swells is governed by individual factors which vary considerably in the different classes of fruits, special precautions must be taken in order to study the effect of one factor, such as acidity or pH. The problem may be approached in several ways, one of which is to take a single sample of fruit of low acidity and add varying quantities of a fruit acid to the covering syrup so that a range of several pH values is obtained for comparison; another is to compare the effect of added acid to fruits of approximately the same natural pH; a third is merely to compare the losses from hydrogen swells in the whole range of fruits, and see whether the pH value is a major determining factor.

The following table shows the results of trials conducted at Campden, and it will be seen that the only fruits which consistently benefited by the addition of acid were sweet cherries (white and dark) and blanchéd prunes. Greengages benefited slightly in some cases, and bilberries were unaffected in the one test carried out. All other fruits—including soaked prunes—were adversely affected by the addition of acid. In the 1933 tests on white cherries recorded in the table the pH values were 3.76, 3.62 and 3.45 respectively; in the 1933 greengages the pH values were 3.36 and 3.08, while in the 1934 greengages they were 3.18 and 2.93. The pH of the other fruits without added acid were as follows: black cherries 4.08, bilberries 3.00, blackberries 3.03, and Victoria plums 2.97. The prunes will be referred to later.

It will be seen that the beneficial effect of acid in canned

EFFECT OF ADDITION OF CITRIC ACID TO SYRUP

STORED AT 95° F.: PERIODS TO REACH 25 PER CENT LOSS

Fruit	Can	Year	No Acid	0.3 per cent acid	0.5 per cent acid
			weeks	weeks	weeks
White Cherries	Lacq'd	1930	24	29	—
„	Plain	1931	6	—	42
„	Plain	1933	19	51*	44
„	Lacq'd	1934	24	—	30
Black Cherries	Lacq'd	1930	28	50	48
Bilberries	Lacq'd	1930	15	15	—
Strawberries	Lacq'd	1930	29	24	—
Blackberries	Lacq'd	1930	34	28	—
Victoria Plums	Lacq'd	1930	24	20	—
Greengages	Lacq'd	1930	13	14	24
„	Plain	1931	62	—	62
„	Plain	1933	48	—	65
„	Plain	1934	45	—	41
Prunes S.	Plain	1932	13	—	—
Prunes B.	Plain	1932	4½	—	—
Prunes S.	Lacq'd	1932	5	3½	—
Prunes B.	Lacq'd	1932	1½	25	—
Prunes S.	Plain	1933	27	18½	—
Prunes B.	Plain	1933	2½	13	—

S.—Soaked. B.—Blanched.

* Only 0.2 per cent of acid was added to this sample.

cherries was fully developed in the cans in which only 0.3 per cent of citric acid had been added; a greater concentration of acid tended to increase the rate of corrosion. Similar results are recorded in the table on page 76, where gelatine as well as citric acid had been added to the syrup. The addition of 0.2 to 0.3 per cent of citric acid only reduced the pH values by about 0.15, and so it would appear to be highly improbable that the change in hydrogen ion concentration was responsible for the pronounced effects observed. The initial inhibiting action would appear to be due to some counteracting effect produced by the added acid on a natural accelerator in the cherries. Once this accelerating action is overcome the behaviour of the canned cherries when further acid is added is similar to that of other fruits—namely, it produces increased hydrogen formation.

That the pH of the canned product is not one of the major factors governing corrosion is further indicated by the following facts. Sweet cherries and pears have the same pH range (about 3.6 to 4.3), yet the former is about the most active fruit and the latter about the least active in promoting hydrogen swells. Bilberries (pH 2.9 to 3.2) and gooseberries (pH 2.7 to 3.2), at the acid end of the scale, have very similar hydrogen ion concentrations, and yet the former fruit has a strong corrosive action on the steel baseplate while the latter gives relatively little trouble in this respect.

The case of canned prunes is an interesting one and has received close attention by Mrak and Richert (30) in California. The figures given in the above table to some extent confirm and extend those of the American workers; they also show the interesting fact that a preliminary soaking of the dried prunes in water overnight reduces their tendency to cause hydrogen swells, the canned soaked prunes in each test doming less rapidly than those in which the prunes had merely received a preliminary short blanch before canning. The pH values in the two cases were the same at pH 3.92. The addition of 0.3 per cent of citric acid to the syrup had an opposite effect in the two cases—it produced acceleration of corrosion with soaked

prunes (pH 3.72) and retardation with blanched prunes (pH 3.63). It seems probable that the prunes lost a strong accelerator by diffusion during soaking—possibly quinic acid, which is mentioned as being present by Kohman and Sanborn (16)—and their behaviour in cans thereafter resembled that of most normal fruits, including their reaction to added acid. The blanched prunes, on the other hand, had the accelerator still present when canned, and benefited by the addition of acid in the same way as sweet cherries. The general indication of the Campden results mentioned above appears to favour the suggestion that the rate of hydrogen formation increases with rise in acidity (as has been shown in laboratory tests on the corrosive action of citric acid on mild steel in the absence of air) but that certain fruits—notably cherries, prunes and greengages—contain specific accelerators of iron corrosion, the effect of which can be counteracted by adding a small quantity of citric acid to the syrups used for canning. The general trend of the evidence appears to be decidedly against the commonly accepted hypothesis that the less acid fruits are more prone to produce hydrogen swells than the more acid by reason of their low acidity.

It may be of interest to note in this connection that Morris (27) has suggested that there may be an optimum pH for each fruit at which its corrosive action is at a minimum.

The effect of adding acids other than citric was also studied. Any differences noted in a test of this type might be due to one of three causes—(a) to a specific effect due to the acid itself; (b) to the presence of inhibitors or accelerators due to the source and method of preparation of the acid; and (c) to the extent of inversion of the sugar syrup produced by the acid. Commercial samples of three fruit acids—citric, malic and tartaric—were compared, all at 0.5 per cent strength. The sample of malic acid gave decidedly better results than the citric, while the tartaric acid was rather less efficient than the latter. The syrups containing tartaric acid were more highly inverted (9 to 20 per cent) than those containing citric or malic acids (5 to 8 per cent), but further tests on syrups highly inverted

(69 to 100 per cent) by citric acid indicated that the extent of inversion was not a factor of major importance. There was not sufficient evidence to justify the singling out of any of the acids mentioned for use in the canning of sweet cherries.

ACCELERATORS AND INHIBITORS

The rate of corrosion may be greatly increased or diminished by the presence of minute traces of certain substances which can act either as accelerators or inhibitors. The presence of such substances in commercial cane and beet sugars, and of sulphur compounds, has already been referred to. Oxygen and oxidizing agents act as accelerators in all classes of fruits.

Colloidal substances such as gelatine, agar-agar and pectin might be expected to act as inhibitors, and consequently the effect they produce when added to canned fruits was examined in these trials. Agar-agar up to a maximum concentration of 0.10 per cent was found to have no appreciable effect when added to canned loganberries, sweet cherries and plums. Pectin, which is naturally present in nearly all fruits, did not produce beneficial results when added to canned loganberries and sweet cherries at a concentration of 0.10 per cent. Gelatine, however, was found to inhibit corrosion at all acidities, as shown in the table; the amount used was 0.2 per cent in the earlier tests and 0.4 per cent in the 1934 tests.

Sulphur in the form of sodium thiosulphate was added at a concentration of only three parts per million of the total contents; it acted as a strong accelerator in the more acid fruits and as a strong inhibitor with sweet cherries.

The accelerators and inhibitors present in commercial cane and beet sugars have not been isolated, but their action indicates that they are probably not sulphur compounds. Certain evidence made it seem possible that the inhibitor in beet sugar might contain an amino-acid group, but 0.05 per cent of amino-acetic acid added to the syrup did not reduce the rate of corrosion in tests on loganberries, sweet cherries, bilberries and plums.

In laboratory tests on the corrosion of strips of mild

EFFECT OF ADDED GELATINE AND SODIUM THIOSULPHATE

STORED AT 95° F.: PERIODS TO REACH 25 PER CENT LOSS

Fruit	Can	Added Citric Acid	Year	Control	Gelatin	Sodium Thiosulphate	pH
		per cent		weeks	weeks	weeks	
Gooseberries	Lacq'd	nil	1933	27	26	9	2.95
Loganberries	Lacq'd	nil	„	19	29	10	2.93
White Cherries	Plain	nil	„	19	32	86	3.76
„	Plain	0.2	„	51	59	64	3.62
„	Plain	0.5	„	44	49	54	3.45
„	Lacq'd	nil	„	17	—	35	3.74
Greengages	Plain	nil	„	48	54	22	3.36
„	Plain	0.2	„	—	79	26	3.26
„	Plain	0.5	„	65	67	21	3.08
„	Lacq'd	nil	„	26	—	20	3.32
White Cherries	Lacq'd	nil	1934	24	26	40	3.67
„	Lacq'd	0.5	„	30	34	39	3.38
Greengages	Lacq'd	nil	„	45	46	27	3.18
„	Lacq'd	0.5	„	38	38	27	2.93

steel in buffered solutions of citric acid containing fifteen parts per million of sulphur as sulphur dioxide, Hoar and Havenhand (10) showed that the accelerating effect of sulphur was considerable at pH 2, but became less as the hydrogen ion concentration was decreased to pH 5, where its action was negligible. At no part of this range did

sulphur inhibit corrosion. In the above table, showing the results of practical canning trials at Campden, it will be seen that sulphur acted as an inhibitor in all the tests on canned cherries and as an accelerator with all the remaining fruits. If the cherry tests are arranged in order of their pH values it will be noted that the inhibiting power decreases progressively as the acidity increases. The experiments were originally planned to show whether there was any critical pH value at which sulphur ceases to function as an accelerator and becomes an inhibitor, and although the pH values of inhibited and accelerated samples did not actually overlap, the difference between cherries and greengages at pH 3.3 to 3.4 was very marked, the former still exhibiting a pronounced inhibition of corrosion with added sulphur and the latter strong acceleration. This evidence strongly favours the view that the inhibiting action of sulphur in canned cherries is specific to the fruit, and is not directly related to the hydrogen ion concentration for all classes of fruits; the sulphur may function as an inhibitor by reducing the activity of a natural accelerator in cherries. Further evidence that inhibition is not associated directly with pH is found in the fact observed by Culpepper and Moon (8) that sulphur accelerates the rate of swelling of canned peaches—a fruit which has the same pH range as sweet cherries. These workers also pointed out that sulphur might act as an inhibitor in double lacquered cans while producing acceleration with similar fruit in plain cans; this has not been confirmed in the Campden tests. Other experiments conducted at Campden showed that sulphur added in widely differing forms, such as allyl isothiocyanate and cystine, gave results very similar in direction, though different in magnitude, to sodium thiosulphate.

The work described in this section has contributed some interesting sidelights on the hydrogen swell problem, and the results would appear to indicate that sulphur compounds have less effect at low acidities, but that the inhibiting action noted in canned cherries is specific to that fruit and is not accounted for merely by its relatively low hydrogen ion concentration. As far as the question of

adding inhibitors to the syrups used for canning is concerned, it may be noted that gelatine is the only edible product which has given satisfactory results. This substance is, however, rather difficult to handle satisfactorily in the cannery, and its effect is not very great. In addition it should be the aim of food packers to use as few "adulterants" as possible, even if they be as harmless as gelatine in the present instance, and consequently canners would be well advised to avoid using this or any other of the inhibitors mentioned.

CANNING PROCESSES

HEADSPACE

The importance of an adequate headspace has been shown on page 56. This is a factor over which the canner is able to exercise control, and failure to ensure that a good headspace is left before closing the can often leads to early trouble from hydrogen swells. A displacement of about one-quarter of an inch on the "toppers" generally gives a final headspace of roughly three-sixteenths of an inch after the cans have been processed and cooled; a larger headspace than this tends to give the consumer the impression that the can is underfilled. Where a good headspace has been allowed the cans may show a predomining life quite 50 per cent longer than that of overfilled cans.

In tests carried out at Campden it was found that canned plums, packed under the standard conditions employed in these experiments, often showed small final headspaces, the volume of the contents after cooling being greater than that of most of the berry fruits. This is a point worth noting, as it is often the case that commercially packed plums also show very little headspace. Canners should consequently pay special attention to the question of headspace in canned plums, as it is quite possible that insufficient care in this direction is one of the reasons for the high rate of loss from hydrogen swells in this class of fruit.

EXHAUST PROCESS

The chief objects of the exhaust process are to expel air

which has been trapped in contact with the fruits and to enable the cans to be closed at a high temperature. It was previously thought that the process also released "air" held in the intercellular parts of the fruits, and thus reduced the oxygen content of the headspace when the cans were closed. Horner (13) has recently shown that this "air" normally consists of a mixture of nitrogen and carbon dioxide in most fruits (apples are possibly an exception) and is almost entirely free from oxygen, so the advantages of the exhaust process are probably confined to the two mentioned above.

The increase in the marketable life of cans consequent upon using an efficient exhaust process was clearly shown in the Campden trials, where cans were treated as follows: (a) filled 170° F., no exhaust; (b) filled 170° F., exhausted six minutes at 190° F. The cans were stored at 95° F. and a 25 per cent loss was recorded in the following times.

Loganberries	No exhaust	—	20 weeks
	Exhaust	—	30 weeks
Damsons	No exhaust	—	17 weeks
	Exhaust	—	45 weeks

The relative merits of a short exhaust at a high temperature (five minutes at 190° F.) and a long exhaust at a lower temperature (ten minutes at 160° F.) were compared. The cans in the latter batches were closed at a temperature about 10° F. lower than those in the former, and the results indicated that the slight advantage recorded in the high temperature tests were chiefly due to the temperature of closure. This was confirmed in subsequent tests, and it was found that no benefit—as far as hydrogen swells were concerned—was obtained by exhausting at a temperature as low as 160° F.

When these trials were first undertaken it was thought that the removal of oxygen from the intercellular spaces of the fruits was one of the chief functions of the exhaust process. Consequently a "double exhaust" process was tested, the first exhaust at 115° to 120° F. being designed to bring about destruction of the intercellular oxygen by

respiration, and the second exhaust at 190° F. being for the purpose of obtaining a high closing temperature. No advantage was gained in any of the lots of fruit packed in this manner.

Another method of producing a vacuum in the cans is to make use of a vacuum closing machine. Closing vacua as high as twenty-four inches were tested in the trials carried out in 1929 and 1930; all the principal fruits were packed in this manner and in some cases the vacuum was applied for a considerable time (up to thirty seconds) in order to withdraw some of the entrapped or dissolved gases before closing. In all cases the effect of subsequent heating during processing was to reduce the final vacua to eight to twelve inches. The rate at which these cans formed hydrogen swells was quite as rapid as that recorded in the cans exhausted in the usual way. An attempt to combine a "respiration" exhaust (115° to 120° F.) with the vacuum closing process was equally unsuccessful in reducing corrosion.

CLINCHING AND CLOSING TEMPERATURE

The mechanical advantage of closing the cans at a high temperature has been referred to on page 56, but the reduction in the oxygen content is also an outcome of the higher closing temperature. When the can passes under the seaming head the space above the contents consists of a mixture of water vapour and air, the proportion of the latter growing less as the surface temperature rises. The effective temperature of closure is easily reduced by a current of cold air striking the can as it is being closed, and consequently the cans should be protected from chilling of this kind between the exhaust box and the closing machine.

One of the best methods of ensuring a high closing temperature is to clinch the cans before exhausting; by this means the ends are attached lightly to the cans, thus preventing serious chilling between the exhaust box and the closing machine. Clinching also enables the cans to be exhausted at a higher temperature, as the attached ends protect the contents from the agitation of the water in the tank.

The effect of the temperature of closure on the rate of formation of hydrogen swells is shown in the following figures, obtained with cans stored at 95° F. until they showed 25 per cent loss.

Loganberries	—	Closed 130° F.	—	22 weeks
		Closed 180° F.		27 weeks
Damsons	—	Closed 130° F.	—	33 weeks
		Closed 180° F.		52 weeks

The advantage of using a clincher is indicated below, where the cans were treated alike, except that the lids were clinched before exhausting in one lot.

EFFECT OF CLINCHING

STORED 95° F.: PERIOD TO REACH 25 PER CENT LOSS

Fruit	Controls	Clinched
	weeks	weeks
Strawberries	18	27
Raspberries	20	25
Loganberries	18	23
White Cherries	39	51
Blackberries	27	33

COOLING

If cans are stacked in bulk while still at a high temperature (120° F. or over) the contents will continue to soften and may eventually be spoilt, but another effect of the high temperature is to accelerate the early stages of corrosion. This may, in extreme cases, reduce the marketable life of the cans quite appreciably, but in the Campden tests there was little difference noted between cans removed from the cooling tank at 130° to 140° F. and others chilled immediately to 34° F.

STORAGE CONDITIONS

TEMPERATURE

The temperature of storage has a very great influence on

the rate at which hydrogen swells form. If it were possible to store cans at 40° F., instead of at the more usual temperature of 55° to 60° F., the life of the cans would be roughly doubled. A storage temperature of about 75° F., on the other hand, would reduce the life to about one-half, and a temperature of 90° F. to about one-quarter. In the Campden trials batches of cans from the same tests were divided into two lots, one being stored at 72° F. and one at 95° F. The following table shows the times required to reach 25 per cent of hydrogen swells in each case.

	STORED 72° F.	STORED 95° F.
Gooseberries	180 weeks	60 weeks
Damsons	140 „	39 „
Loganberries	110 „	32 „
Strawberries	100 „	30 „
Blackberries	90 „	35 „
Raspberries	90 „	28 „
Cherries (White)	62 „	23 „
Blackcurrants	60 „	22 „
Plums (Persnore)	45 „	17 „
Bilberries	36 „	16 „

It will be seen that the cans stored at 72° F. showed about three times the life of those stored at 95° F.

AGITATION

When cans are transported over long distances they are being subjected to some form of agitation most of the time. This rocking or shaking might be expected to cause depolarization to take place, the bubbles of hydrogen being removed particularly at points where the moving surface of the liquid touched the corroding areas. This action would accelerate corrosion.

The tests carried out at Campden on this subject were designed to show the effect of intermittent agitation over a long period, the cans being held in trays which could be rocked about a horizontal axis through an angle of about thirty degrees. The rocking movement was carried out twice daily for periods of about five to ten minutes. Similar

sets of cans were held stationary as "controls." In neither of the two tests did the agitated cans form hydrogen swells more rapidly than those which were allowed to remain stationary.

In this connection it might be mentioned that Carrasco (6) considers that prolonged agitation of cans accelerates corrosion, but it is possible that his remarks refer to continuous agitation and not to the intermittent movement described above.

STORAGE IN HOT CLIMATES

The temperature conditions in the hot room at Campden (95° F. constant) were chosen deliberately to represent the worst average temperatures likely to be met with in the tropics. In 1932 the Admiralty kindly offered to store and examine batches of cans at the Victualling Yards at Malta and Hongkong, and sets of cans were sent from the Research Station, "controls" being placed in the Campden hot room at the same time. The results showed, as might have been expected, that the Campden storage conditions were much more severe than those in either of the naval depots.

At Malta the cases were kept near a window on the south-western side of the store out of the direct rays of the sun. A maximum temperature of 110° F. was recorded at the end of July 1933, and a minimum temperature of 50° F. was recorded in late February 1933. The averages of the daily maximum and minimum readings were as follows for three-monthly periods:

	MAX.	MIN.
December to February inclusive	69°	57° F.
March to May ,,	78°	62° F.
June to August ,,	96°	76° F.
September to November ,,	85°	71° F.

The winter conditions were therefore somewhere near those normally ruling in England; the summer conditions were considerably cooler than those in the Campden hot room.

The Hongkong temperatures were not obtained, but

they probably exceeded those in Malta by five or ten degrees. The results of the full tests were as follows:

Fruit	Period to Reach 25 per cent Loss		
	Campden	Malta	Hongkong
	weeks	weeks	weeks
Strawberries	27	—	80
Raspberries	20	62	70
Victoria Plums	19	42	26

The strawberries at Malta had shown no losses after fifty-five weeks, and were then removed.

CONCLUSIONS AND RECOMMENDATIONS

GENERAL COMMENTS

In the preceding pages the problem of the hydrogen swell has been discussed both in its "immediate" or practical aspect, and also as a problem in metallurgical chemistry. Suggestions relating to the composition of the baseplate, put forward by research workers on the metallurgical side, have been mentioned, but it seems unlikely that any great improvement in this direction can be brought about until further knowledge of the effect of minute impurities in the steel baseplate is available, and until such knowledge can be effectively put into practice. In the meantime information has been accumulated which shows the influence of each of the main commercial operations—from those of the can-maker to those of the persons responsible for the storage of the filled cans—on the rate at which hydrogen swells form. There appears to be reasonable justification for hoping that the present losses can be cut down considerably by developing methods of lacquering the cans so as to cover the areas known to be responsible for the greater part of the corrosion. Such processes will take some time to put into full commercial practice, but when this stage is reached the canner should be relieved of much of the worry at present occasioned by a heavy "carry-over" from one season to the next.

Another point which might be mentioned at this stage—and which was emphasized in the Introduction—is that the hydrogen swell is only one aspect of the corrosion problem. Discoloration of the fruits and cloudiness of the syrups are points which bring discredit to the industry—a discredit which produces a cumulative effect, in that it tends to hold up stocks in the shops and thus increase the extent of the deterioration still further. More complete protection of the seams and expansion rings would greatly retard the rate at which this form of deterioration takes

place, and so should eventually reduce very greatly this justifiable cause for complaint. Even if this desirable state of affairs is realized in the near future canners should still make every effort to store their products at as low a temperature as possible, for temperature alone—as distinct from the accelerating effect it has on corrosion—produces changes in canned fruits. Tests on fruits packed in all-glass bottles have shown that a low temperature of storage preserves the full flavour and arrests the slow change of colour that would otherwise occur, while a high storage temperature favours the loss of natural flavour and the production of a slightly bitter taste and a dull colour.

INDIVIDUAL FRUITS

GOOSEBERRIES

These are often packed in plain cans, and have a slightly better colour in such cases. If they have to be stored for a long period, or at a high temperature, lacquered cans should be used, as the tin content of the canned product is thus kept at a low figure. Normally they do not form hydrogen swells easily, even in lacquered cans, but samples differ quite considerably in this respect. Minute traces of sulphur compounds, such as may arise from the residue of lime-sulphur sprays used by the grower to protect the fruit against mildew, may greatly accelerate the formation of hydrogen swells. Perforations are uncommon.

STRAWBERRIES

Double lacquered cans must be used for this fruit. Many canners do not exhaust strawberries at as high a temperature as other fruits, so special care should be taken to leave an adequate headspace. The susceptibility to hydrogen swells is variable, but about the same as that found in most other soft fruits. Traces of sulphur sometimes adhere to the berries through the grower dusting with sulphur after the fruit has formed—this greatly accelerates corrosion. Perforation seldom follows doming very rapidly in the strawberries packed in England.

RASPBERRIES

Double lacquered cans are used. This fruit takes the heat out of the syrup rapidly during the exhaust process, and so the cans are often closed at a lower temperature than those of most other fruits. They are one of the worst berries (except bilberries) for causing hydrogen swells, though generally better than most stone fruits in this respect. Perforations often follow on doming rather closely.

LOGANBERRIES

Double lacquered cans are used. The effect of corrosion on the exposed areas of metal in the seams and on the expansion rings is generally rather noticeable; in this respect they resemble raspberries and blackcurrants. They usually show fewer hydrogen swells than raspberries and seldom give much trouble from perforations.

BLACKCURRANTS

These are packed in double lacquered cans and rapidly show severe attack on areas of exposed metal. Hydrogen swells form rather rapidly, but perforations are not common until the cans have been stored for a long period. Currants tend to swell on cooking, and care should be taken to avoid overfilling.

BLACKBERRIES

The cultivated blackberry (which is the only type canned on a large scale) is packed in double lacquered cans and is generally slow in producing hydrogen swells. Perforations often occur fairly soon after doming. The hedge blackberry is much less acid than the cultivated types, and seems to promote hydrogen swells more rapidly.

BILBERRIES

The bilberry (or blueberry, or blaeberry) also requires a well lacquered can. It forms hydrogen swells more readily than any other berry, and the cans perforate very rapidly. Though its pH may be as low as pH 2.9 this

probably varies a great deal, and an increase in resistance against hydrogen swells has been reported in cases where a small quantity of citric acid has been added to the syrup.

CHERRIES

Sweet cherries, both white and dark, readily promote hydrogen swells. The white varieties may be packed in plain cans (they do not often show a high tin content in such cases) but there seems to be little advantage thus gained as far as hydrogen swells are concerned. The addition of a quarter to a half ounce of citric acid per gallon of syrup greatly reduces the rate of hydrogen formation. Visible signs of corrosion round the seams of lacquered cans is very slight; perforation does not follow doming very rapidly. Accidental traces of sulphur compounds do not accelerate corrosion but tend to produce a foreign flavour.

GREENGAGES

Plain cans may be used, but lacquered are generally preferred. The rate of formation of hydrogen swells is lower in plain cans, and varies greatly in different lots of fruit. With ripe samples some advantage may be gained by adding about a quarter to a half ounce of citric acid to the syrup. A good headspace should be allowed.

GOLDEN PLUMS

The Pershore plum is often packed in plain cans and gives less trouble from hydrogen swells in these than in lacquered cans. The same remarks apply to this fruit as to gooseberries in regard to tin content. The less ripe fruits produce hydrogen swells a little more slowly than the firm-ripe, but the difference is insufficient to counterbalance the better appearance of the latter. Acid should not be added, and special attention should be given to prevent overfilling. Holding the plums for several days before canning does not appear to affect subsequent doming.

RED PLUMS

Double lacquered cans are used. Red plums generally

do not give heavier losses than the yellow varieties, but it is often noticeable that hydrogen swells form rapidly in canned Czars. The headspace and closing temperature should be watched carefully.

VICTORIA PLUMS

These are packed in double lacquered cans and generally produce hydrogen swells at about the same rate as Pershore plums, but, as with the yellow variety, the results vary greatly. Attention should be given to the closing temperature and headspace.

DAMSONS

Double lacquered cans are used. Of all types of plums these generally give least trouble from hydrogen swells, and are also slow in producing perforations. Occasionally samples show a faster rate of corrosion, but the variation in this respect seems to be less than in most fruits.

APPLES

These are canned in "solid pack" form in plain A.10 cans. The slices should be allowed to soak overnight in a dilute brine—this reduces the oxygen content of the headspace gases. A reasonable headspace should be allowed, and the closing temperature should be about 150°F. Higher closing temperatures cause panelling of the sides of the cans after cooling. Hydrogen swells do not form very readily; perforation occasionally takes place before doming.

PRUNES

Dried prunes canned in syrup produce hydrogen swells very rapidly. The best way to overcome this is to soak the prunes overnight in water, but this process gives them a paler colour and is seldom used in commercial practice. If the prunes are merely blanched and then canned it is necessary to add a small quantity (0.2 to 0.3 per cent) of citric acid to the syrup used for covering. A long exhaust at a high temperature (200° to 210° F.) should be given. Plain cans are generally recommended, but their advan-

tage was not very pronounced in tests conducted at Campden. This product should be sold as soon as possible after canning.

APRICOTS

Fresh apricots are packed in plain cans. The usual precautions regarding headspace and closing temperatures should be observed. This fruit seldom gives serious trouble from hydrogen swells unless the cans are stored for a long period or at a high temperature.

PEACHES

These are packed in plain cans and show relatively slight losses from hydrogen swells. On the whole they appear to be rather better in this respect than gooseberries packed in similar types of cans. They should be well exhausted and closed at a high temperature with an adequate headspace.

PEARS

This fruit seems to give as little trouble as any, and losses from hydrogen swells seldom occur until the cans have been in store for a long period. Plain cans are used; a good headspace and high closing temperature should be given.

PINEAPPLES

The losses from hydrogen swells are seldom great with pineapples packed in plain cans. The latter should be well exhausted and given a good headspace.

GRAPEFRUIT

Losses from hydrogen swells are apt to be considerable unless the cans are given a very thorough exhaust at a high temperature; the use of a clincher is an advantage in this respect. The fruit is packed in plain cans.

RHUBARB

Though this is not a fruit, it may be included in the present list. Rhubarb has a very violent action on the tin

coating, and very well lacquered cans *must* be used. A preliminary soaking of the rhubarb sticks overnight reduces the subsequent rate of corrosion. If the usual precautions are taken regarding headspace and temperature of closure the losses from hydrogen swells are seldom high.

TROPICAL FRUITS

Little is known of the tendency for tropical fruits, such as mangoes, guavas, litchis and papaws to promote hydrogen swells. In some cases acid may have to be added to these fruits, to increase their hydrogen ion concentrations for purposes of sterilizing the fruits at boiling point, but the effect of such additions on the liability to form hydrogen swells is still unknown. Plain cans may be used for the fruits mentioned.

PRECAUTIONS AND REMEDIES

TINPLATE

(1) The use of rimming steels (as recommended by Hoar) which should also be low in sulphur content, and with a copper-sulphur ratio greater than two. Freedom from inclusions of massive cementite.

(2) The application of improved methods of tinning, so as to reduce porosity. This subject forms part of an investigation by the International Tin Research and Development Council which is still in progress.

CAN-MAKING

(3) Special care given to the stamping out of ends and formation of seams, so as to keep the area of exposed steel down to a minimum.

(4) The use of ends with expansion rings designed so as to give a high doming pressure without interfering unduly with the other functions of the rings.

(5) The development of a new process of lacquering with the object of protecting completely those areas in which steel has been exposed during the can-making process.

RAW MATERIALS

(6) The use of beet sugar (as recommended by Morris

and Bryan) where possible. Unblued sugar is essential.

(7) The addition of $\frac{1}{4}$ to $\frac{1}{2}$ ounce of citric acid per gallon of syrup for sweet cherries. The same quantity is sometimes of benefit with ripe greengages and bilberries.

(8) Plain cans for gooseberries, yellow plums and greengages, where the time of storage is unlikely to be long, or the temperature of storage high. White cherries do not benefit greatly by being packed in plain cans.

CANNING PROCESSES

(9) The use of a clincher before the cans pass to the exhaust box.

(10) An efficient exhaust process, giving a high closing temperature.

(11) An adequate headspace—at least one-quarter of an inch before the ends are in position.

(12) The cans cooled to at least 100° F. before stacking.

TRANSPORT AND STORAGE

(13) The prevention of unnecessary shaking or rolling during transport.

(14) Storage under as cool conditions as possible.

REFERENCES

(1) ADAM, W. B.: Diffusion of Acid and Sugars During Processing and Storage of Canned Fruits. *Ann. Rept. of the Fruit and Veg. Presvn. Res. Stn., Campden, Glos.* 1933-34, page 42.

(2) ADAM, W. B., and STANWORTH, J.: Investigation of the Pressures Produced in Cans During Sterilization. *Ann. Rept. of the Fruit and Veg. Presvn. Res. Stn., Campden, Glos.* 1931-2, page 44.

(3) BRYAN, J. M.: The Effect of Traces of other Metals on the Rate of Corrosion of Tin by Citric Acid. *Rept. of the Food Investigation Board*, 1932, page 163.

(4) BRYAN, J. M.: The Corrosion of Tin. *Rept. of the Food Investigation Board*, 1934, page 117.

(5) BUCHANAN, E. S., and SCHRYVER, S. B.: *Rept. of Inspector of Foods, Local Government Board*, 1908.

(6) CARRASCO, O.: Corrosion Phenomena in Tinned Sheet Containers. *Food*, November 1934, 4, 48.

(7) CHAPMAN, A. C.: Action of Tartaric Acid on Tin in the Presence of Oxygen. *Jour. Chem. Soc.*, 1913, 103, 775.

(8) CULPEPPER, C. W., and MOON, H. H.: Sulphur Spray Residues and the Swelling of Canned Peaches. *Canning Age*, 1928, 9, 461.

✓ (9) HOAR, T. P.: The Electrochemical Behaviour of the Tin-Iron Couple in Dilute Acid Media. *Trans. Faraday Soc.*, 1934, 30, 472.

(10) HOAR, T. P., and HAVENHAND, D.: Factors Influencing the Rate of Attack on Mild Steels by Typical Weak Acid Media. *Jour. of the Iron and Steel Inst.*, 1936, 133, 239P.

(11) HOARE, W. E.: Tin-Iron Alloy in Tinplate with Notes on Some Imperfections. *Jour. of the Iron and Steel Inst.*, 1934, 129, 253.

(12) HORNER, G.: The Internal Rusting of Cans. *Ann. Rept. of the Fruit and Veg. Presvn. Res. Stn., Campden, Glos.* 1932-3, page 43.

(13) HORNER, G.: Gases in Canned Fruits. *Ann. Rept. of the Fruit and Veg. Presvn. Res. Stn., Campden, Glos.*, 1933-4, page 50.

(14) HOTHERSALL, A. W., and BRADSHAW, W. N.: Methods of De-tinning Tinplate for Examination of Thickness and Continuity of Alloy Lacquer. *Jour. of the Iron and Steel Inst.*, 1936, **133**, 225 P.

(15) HOTHERSALL, A. W., and PRYTHERCH, J. C.: A study of the Origin of Porosity in the Tin Coating of Tinplate. *Jour. of the Iron and Steel Inst.*, 1936, **133**, 205 P.

(16) KOHMAN, E. F., and SANBORN, N. H.: Isolation of Quinic Acid from Fruits. *Ind. and Eng. Chem.*, 1931, **23**, 126.

(17) LUECK, R. H., and BLAIR, H. T. Corrosion in the Tin Can. I.—Electrochemical Relations of Iron and Tin. *Trans. Ann. Electrochem. Soc.*, 1928, **54**, 257.

(18) McCONKIE, J. E.: Influence of Copper Bearing Steels on Can Corrosion. *Canner*, 1930, **70** (No. 8), 13.

(19) MORRIS, T. N., and BRYAN, J. M.: The Corrosion of the Tinplate Container by Food Products. *Dept. of Sci. and Indus. Res.—Food Investigation. Special Report No. 40*, 1936.

(20) MORRIS, T. N., and BRYAN, J. M.: Second Report on the Corrosion of the Tinplate Container by Food Products. *Dept. of Sci. and Indus. Res.—Food Investigation. Special Report No. 44*, 1936.

(21) MORRIS, T. N.: The Diffusion of Hydrogen through Mild Steel Sheet during Acid Corrosion. *Jour. Soc. Chem. Ind.*, 1935, **54**, 7T.

(22) MORRIS, T. N.: The Corrosion of Steel and Tinplate by actual Extracts of Fruits. *Rept. of the Food Investigation Board*, 1934, page 180.

(23) MORRIS, T. N.: The Effect of Sugar on the Corrosion of Tinplate in Canning. *Rept. of the Food Investigation Board*, 1935, page 165.

(24) MORRIS, T. N.: Inhibitors and Accelerators. *Rept. of the Food Investigation Board*, 1930, page 119.

(25) MORRIS, T. N.: Inhibitors and Accelerators of Corrosion. *Rept. of the Food Investigation Board*, 1931, page 191.

(26) MORRIS, T. N.: The Corrosion of Steel and Tinplate by Acids other than Citric. *Rept. of the Food Investigation Board*, 1932, page 170.

(27) MORRIS, T. N.: *Principles of Fruit Preservation*, page 117. Chapman and Hall Ltd., London, 1933.

(28) MORRIS, T. N.: Variation in the Rate of Corrosion of Tinsplate. *Rept. of the Food Investigation Board*, 1931, page 183.

(29) NATIONAL CANNERS' ASSOCIATION RESEARCH LABORATORY. Canned Food Containers. A Study with Special Reference to the Influence of the Steel Base on Resistance to Perforation. *N.C.A. Bull. No. 22-L.*, December 1923.

(30) MRAK, E., and RICHERT, P. H.: The Swelling of Canned Prunes. *Univ. of California, Agric. Expt. Stn. Bull. No. 508*, 1931.

Other papers dealing with various aspects of the corrosion of tinsplate by fruit acids are given in the following Bibliography.

PAPERS DEALING WITH THE CORROSION OF TINPLATE AND HYDROGEN SWELLS

AUTHOR	REFERENCE	SUBJECT
ADAM, W. B.	<i>Food Manufacture</i> , 1931, 6, 103.	General discussion of lacquering in relation to corrosion and discoloration.
BRYAN, J. M.	<i>Trans. Faraday Soc.</i> , 1931, 27, 606.	Effect of pH on corrosion of tin.
BRYAN, J. M.	<i>Rept. of Food Invest. Board</i> , 1930, p. 109.	Rough surface of plate increases corrosion.
BRYAN, J. M.	<i>Rept. of Food Invest. Board</i> , 1931, p. 172.	Ferric ion increases rate of corrosion of steel in presence of oxygen.
BRYAN, J. M. & MORRIS, T. N.	<i>Rept. of Food Invest. Board</i> , 1932, p. 197.	Effect of metals on the colour of certain red and purple fruits.
CHEFTEL, H.	<i>Établts. J-J. Carnaud, Lab. de Recherches Biologiques—Bull. No. 5.</i>	General survey of theoretical and practical problems of can corrosion.
CLARKE, S. G.	<i>Analyst</i> , 1934, 59, 1525.	Method of determining thickness of tin coatings.
CLOUGH, R. W. & CLARK, E. D.	<i>Canning Age</i> , 1925, 6, 490	Canning tests on rhubarb. Soaking overnight and then blanching gives fewest losses. Lacquering retards hydrogen formation.
CLOUGH, R. W., SHOSTROM, E. E. & CLARK, E. D.	<i>Canning Age</i> , 1924, 5, 531	Lime-sulphur spray residues in canned gooseberries accelerate hydrogen formation. Less trouble with double lacquered than with plain cans.
CLOUGH, R. W., SHOSTROM, E. E. & CLARK, E. D.	<i>Canning Age</i> , 1930, 11, 402.	Effect of sulphur in fruits of different acidities.
CULPEPPER, C. W. & MOON, H. H.	<i>Canner</i> , 1929, 68, (No. 18), 23.	Corrosion of iron and tin in fruit juices.
CULPEPPER, C. W. & MOON, H. H.	<i>Canner</i> , 1929, 68, (No. 9), 13.	Action of fruit acids on tinplates.
CULPEPPER, C. W. & MOON, H. H.	<i>Canning Age</i> , 1928, 9, 619	Detinning effect of nitrates—mainly occurs at high acidities.

- CULPEPPER, C. W. & CALDWELL, J. S. *J. Agric. Res.*, 1927, 35, 127. Discoloration of fruits containing anthocyanin pigments by interaction with tin.
- DRING, G. *Chem. and Ind.*, 1934, 53, 1013. Description of phenolic resins for lacquering.
- HANSON, D. & SANDFORD, E. J. *J. Inst. Met.*, 1935, 56, 43. Effect of metallic impurities in tin (Bi, Mn, and Al).
- HANSON, D., SANDFORD, E. J. & STEVENS, H. *J. Inst. Met.*, 1934, 55, 341. Effect of metallic impurities in tin (Ag, Fe, Ni and Cu).
- HIRST, F., & ADAM, W. B. *Univ. of Bristol Res. Stn. Campden, Canners' Bul. No. 1 (and Supplements)*, 1930, 1931 and 1933. Experiments on hydrogen swells in English canned fruits.
- HOARE, W. E. & CHALMERS, B. *J. Iron and Steel Inst.*, 1935, 132, 135. Examination of surface of tinplate.
- HOTHERSALL, A. W. & BRADSHAW, W. N. *J. Soc. Chem. Ind.*, 1935, 54, 320T. Superimposed electrodeposition of tin on tinplate.
- JONES, W. D. & HOARE, W. E. *J. Iron and Steel Inst.*, 1934, 129, 273. Microscopic examination of iron-tin reaction products.
- KOHMAN, E. F. *Canning Age*, 1928, 9, 227. Hydrogen swells in stone fruits. Accelerating effect of crushed cherry pitts.
- KOHMAN, E. F. *Canning Age*, 1927, 8, 234. Rate of corrosion in cans made from coke and charcoal plate.
- KOHMAN, E. F. *Ind. & Eng. Chem.*, 1923, 15, 527. Oxygen accelerates corrosion in canned apples.
- KOHMAN, E. F. *Canning Age*, 1925, 6, 191. Effect of oxygen, natural colouring matters and storage temperatures on corrosion.
- KOHMAN, E. F. *Canner*, 1929, 68, (Convention No.), 147. Use of chrome-nickel steels for cans.
- KOHMAN, E. F., & SANBORN, N. H. *Ind. & Eng. Chem.*, 1924, 16, 290. Lacquering, oxygen and natural colouring matters accelerate corrosion.
- KOHMAN, E. F., & SANBORN, N. H. *Ind. & Eng. Chem.*, 1927, 19, 514. Increased coating of tin-iron alloy does not lengthen serviceable life of cans.
- KOHMAN, E. F., & SANBORN, N. H. *Ind. & Eng. Chem.*, 1928, 20, 176. Tin is anodic to iron in canned fruits.
- KOHMAN, E. F., & SANBORN, N. H. *Nat. Canners' Assn. Bull.* 23-L. 1929. Results of canning tests stored at 32°, 50°, 70° and 97° F.
- KOHMAN, E. F., & SANBORN, N. H. *Canning Age*, 1928, 9, 381. General discussion of electrochemical aspects of can corrosion.
- KOHMAN, E. F., & SANBORN, N. H. *Ind. & Eng. Chem.*, 1933, 25, 920. Addition of fruit acid to canned prunes reduces loss from hydrogen swells.
- MACNAUGHTAN, D., CLARKE, S. G., & PRYTHERCH, J. C. *J. Iron & Steel Inst.*, 1932, 125, 159. Methods of determining the porosity of tinplate.
- MANTELL, C. E., & LINCOLN, E. S. *Canning Age*, 1926, 7, 847. Causes of etching and perforation. Mentions reversible potential of tin-iron couple.
- MORRIS, T. N., & BRYAN, J. M. *Trans. Faraday Soc.*, 1933, 29, 1207. Inhibiting action of tin on corrosion of mild steel.
- PELLERIN, A., & LASAUSSE, E. *Chim. et Ind.*, 1931, 25, 304. French work on corrosion of various products. Sodium phosphate retards corrosion.

✓ 11/23.6.80
a-8 84

C. F. T. R. I. LIBRARY, MYSORE

✓ 2440

CFTRI LIBRARY, MYSORE - 570 013

Acc. No. 3007

Call No. F8,39N:6 N37

Please return this publication on or before the last due date stamped below to avoid
Incurring overdue charges.

To be issued from: ~

DUE DATE	RETURNED ON	DUE DATE	RETURNED ON
1.10.05	1.11.05		

Acc. No. 3007

39N:6;Z1

(F) N37

swells

uits

